

FINAL REPORT

Metal and Oxide Additives as Agents for Munitions Self-Remediation

SERDP Project WP-1623

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ABSTRACT

Munitions material released into the environment as low-order detonation debris or unexploded ordnance represents potential long-term sources of contamination on training ranges. The objective of this pioneering investigation is to evaluate the effectiveness of multiple additives to initiate explosives degradation upon environmental exposure. Achieving substantial degradation without deleterious impact on munitions performance presents the most severe constraint.

Two formulations were evaluated: PBXN-107 and Composition-B. The PBXN was amended with 5, 10, and 15 weight-% of powdered iron, iron-nickel, or modified TiO_2 . Composition-B was amended with 5 volume-% of the same iron or TiO_2 , as well as sodium dithionite. ARDEC prepared PBXN mixtures and conducted essential safety and stability tests. ERDC prepared Composition B mixtures and evaluated all self-remediation potentials in triplicate column experiments under laboratory conditions.

Self-remediation was not strongly evident for the formulations and conditions considered. Chemical incompatibility of the additives with binder components compromised the PBXN results, but no evidence of RDX degradation was detected. Impact tests reveal a reduction in drop height for amended PBXN, though no reactions were detected in BAM and ABL friction tests, or electrostatic tests. For Comp-B, chemical reduction of TNT to the 4-amino-DNT intermediate was observed with the dithionite and, to a lesser degree, iron amendments. A small increase in TNB, a common photodegradation product of TNT, was observed with TiO_2 -amended Comp-B. As little as $\frac{1}{4}$ vol% Fe is sufficient for potential magnetic collection of particles. This investigation was successful in elucidating multiple challenges to be resolved for successful explosives self-remediation.

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List of Acronyms

Technical Acronyms (alphabetical, numerical by acronym):

HMX: octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine

HPLC: High-Performance Liquid Chromatography

PBXN-107: Polymer Bound eXplosive Number 107, which contains 86% RDX and 14% binder

SEM-EDX: Scanning Electron Microscope –Energy Dispersive X-ray (analytical equipment)

TNB: 1,3,5-trinitrobenzene

TNT: 2,4,6-trinitrotoluene

RDX: hexahydro-1,3,5-trinitro-1,3,5-triazine

4A-DNT: 4-amino-4,6-dinitrotoluene

Organizational Acronyms

ARDEC: U.S. Army Armament Rearch, Development & Engineering Center

EL: Environmental Laboratory, ERDC

ERDC: U.S. Army Engineer Rearch & Development Center

GSL: Geotechnical and Structural Laboratory, ERDC

Keywords

self-remediation, PBXN-107, Composition B, TNT, RDX, carbonyl iron, ZVI, carbonyl iron-nickel, anatase, TiO₂, sodium dithionite, photocatalysis, chemical reduction, NaOH, magnetic

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The PBXN preparation and testing was conducted at ARDEC under the administrative guidance of Reddy Damavarapu. The Comp-B preparation and all self-remediation testing was conducted at ERDC Environmental Laboratory under the administrative guidance of Dr. Richard F. Lance (EP-P Chief), Dr. Richard E. Price (EPED Division Chief), and Dr. Beth Fleming (EL Chief).

OBJECTIVES

The primary objective of this proof-of-principle investigation is to quantify the effectiveness of multiple additives designed to promote explosives degradation upon exposure to environmental conditions. The primary working hypothesis is that small amounts of non-explosive amendments will at least initiate degradation of RDX and TNT upon exposure to light and/or water. Self-remediation must be achieved without substantial deleterious impact on munitions performance, safety, or storage, thereby presenting a severe constraint on additive selection and proportion. These objectives are designed to address issues put forward in the WPSON-08-04 statement-of-need for Self-Remediating Munitions.

This project consists of two phases with distinct tasks. The original tasks, designed as a limited-scope investigation focused on amendments to PBXN-107, included the following:

- Characterize the effectiveness of powdered, carbonyl iron and iron-nickel alloy as agents for the chemical reduction of RDX, and
- Characterize the effectiveness of powdered, WO_3 -doped, anatase, titanium dioxide (TiO_2) as a photocatalyst for RDX degradation.

The results of the PBXN-107 self-remediation experiments were unsatisfactory in that no substantial evidence of RDX degradation was demonstrated. However, these results were compromised by the variable condition of the test samples arising from an apparent interference of the amendments with proper curing of the acrylic binder. A supplemental effort was undertaken to assess self-remediation amendments to Composition B (Comp-B) through the following tasks:

- Demonstrate the effectiveness of powdered carbonyl iron and sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) as agents for the chemical reduction of TNT and RDX, and
- Demonstrate the effectiveness of powdered, WO_3 -doped anatase as an agent of TNT and RDX photocatalysis.

Discovery of a fieldable, self-remediation technology for any munitions would be a lofty goal for this modest effort at the earliest stages of development. The goal of this pioneering investigation is to *begin* the exploration of alternative self-remediation amendments for explosives. A secondary objective is to identify some of the technical challenges that will require further exploration and resolution before self-remediation amendment technologies can be field-tested and successfully implemented.

The methods explored here do not directly address self-remediation of intact UXOs, which would have minimal environmental exposure. The immediate focus is on fully exposed explosives. However, it is conceivable that some of the aphotic methods could be adapted for intra-munitions diminution or disablement.

BACKGROUND

Problem Description

SERDP Weapons Systems and Platforms WPSO-08-04 identified a need “to develop approaches to reduce or mitigate the release of hazardous energetic materials into the environment when munitions do not perform as intended.” Unexploded ordnance (UXO) and low-order detonation debris represent the primary classes of underperforming munitions. The SON called for development of methods to “encourage physical, chemical, or biological degradation of energetic materials into benign products within the munition if it fails to function or in the environment if energetic materials are released.”

Munitions material released into the environment as low-order detonation debris or breached unexploded ordnance (UXO) represents a long-term source of explosives and associated contaminants on training ranges and battlefields. Dissolution and transport of munitions-associated compounds into the soil and subsurface pose a potential environmental risk and would dramatically escalate any restoration costs.

Warfighter training is a high DoD priority (TRADOC, 2005). Development of reliably self-degrading, “fire-and-forget” munitions would have clear relevance to the training mission as it would permit attention and resources to focus on training rather than potential environmental impacts or cleanup.

Uncontrolled detonation of UXOs on ranges would pose a potential risk to military personnel. In regions of conflict, this detonation risk extends to civilians, including children, with the additional threat of a UXO being recovered by enemy combatants for use in improvised explosive devices (IEDs). An improved munitions detonation rate is the obvious preferred solution, but fail-safe mechanisms for the prompt, post-deployment deterioration of explosives could diminish explosive hazards and nefarious re-use.

Self-Remediation Technologies

Self-remediation is a relatively new and evolving concept, requiring clear definition by proponents. Practicable self-remediation technologies do not yet exist for munitions. Historically, the term has been applied to what is now more commonly known as natural attenuation or the ability of an ecosystem to recover from anthropogenic disturbance. In reference to low-order detonation fragments, as in the present investigation, self-remediation would be the complete or partial degradation of munitions explosives initiated only upon environmental exposure. No further field treatment would be required to address potential environmental risks. In practice, exposure to sunlight and/or sufficient liquid water would be the most obvious environmental triggers of self-remediation processes.

Self-remediation of explosives in detonation fragments may be realized when either: (1) new, high explosives are developed that degrade rapidly to environmentally benign products, *i.e.*, green explosives, or (2) stable and compatible amendments are discovered or developed such that very low volume fractions can at least initiate the degradation the explosives. Development of an effectively insoluble explosive also might resolve the environmental risk, but uncontrolled detonation or deflagration risks would remain. In the most general terms, self-remediation involves an engineered treatment *within the source material* that is triggered by environmental exposure, thereby minimizing the considerable effort and expense of plume delineation and cleanup.

Self-remediation of explosives isolated within an intact UXO represents a potentially greater design challenge. Presuming that the explosives charge remained isolated from the environment, self-remediation would have to expose explosives to water (or another reagent) by either drawing it in from the environment or releasing it within the munition, perhaps at the time the weapon is armed immediately prior to deployment. Of course, self-remediation reactions initiated by an internal release would have to be slow enough not to interfere with, or induce, detonation.

Established degradation mechanisms for one or more of the explosives constituents are rational starting points in the development of self-remediation technologies. RDX (1,3,5-trinitro-1,3,5-triazine) and TNT (2,4,6-trinitrotoluene) – two of the most common military high explosives – are highly susceptible to a wide range of environmental transformation reactions, including abiotic or microbially mediated chemical reduction, photo-oxidation, alkaline hydrolysis, and surface-catalyzed reactions. The transformation products tend to be more susceptible to subsequent attenuating reactions such as continued biodegradation or humification (McGrath 1995).

Explosives Formulation Selection

The self-remediation experiments detailed here involve two explosives formulations: PBXN-107 and Composition B. PBXN-107 is a plastic-bonded explosive (PBX) containing only RDX (86 mass-%) with an acrylic binder (components detailed in Table 1). PBXN-107 has a density of approximately $1.64 \text{ g}\cdot\text{cm}^{-3}$ and a detonation velocity of $8.120 \text{ km}\cdot\text{s}^{-1}$ [$5.046 \text{ mi}\cdot\text{s}^{-1}$] (Persson *et al.* 1993). Composition B (Comp-B) contains a mixture of RDX and TNT (60:40 mass proportion, respectively), commonly with a wax binder (~1%). Comp-B has a bulk density of about $1.65 \text{ g}\cdot\text{cm}^{-3}$ and a detonation velocity of $7.800 \text{ km}\cdot\text{s}^{-1}$ [$4.847 \text{ mi}\cdot\text{s}^{-1}$] (Persson *et al.* 1993; Meyer 1981). For reference, the speed of sound at sea level is $\sim 0.34 \text{ km}\cdot\text{s}^{-1}$.

The PBXN-107 formulation was selected for evaluation because RDX is the high explosive of greatest environmental concern in groundwater due largely to: (a) its wide usage, and (b) its effectively conservative nature under conditions typical in otherwise uncontaminated groundwater. PBXN-107 was cited explicitly in the SERDP statement of need (WPSON-08-04) as the preferred formulation in BLU-97 Combined Effects Bombs. High dud rates in bomblet submunitions present safety and environmental risks on training ranges and battlefields. The immediate focus is on munitions fragments exposed to environmental conditions, though lessons learned may be adaptable to the engineered deterioration of explosives within UXO. Finally, preparation of PBXN formulations could be done near room temperatures and pressures, thereby reducing any potential alteration of the amendments or hazards associated with melt or pressure casting.

The Comp-B formulation was selected because it is one of the most widely used formulation in military high explosives. The presence of TNT in Comp-B permits assessment of additional potential self-remediation reactions induced by the amendments. PBXN-107 has largely replaced Comp-B in the most recent model IM BLU-97 munitions.

Common high explosives such as RDX and TNT dissolve slowly from munitions upon environmental exposure, and can act as a long-lived source of soil and groundwater contamination. Natural soils vary widely in their capacity to attenuate nitramine and nitroaromatic contaminants. Strongly reducing, organic rich, and microbially active soils tend to be relatively effective, natural reactive barriers to explosives transport. However, explosives solutes can pass through less reactive soils or through preferential flow paths to impact

underlying aquifers. RDX, in particular, is effectively conservative under the aerobic and oligotrophic conditions typical of uncontaminated aquifers. Thus, engineered initiation of degradation processes proximal to the energetics release points is highly preferable and the ultimate goal of this investigation.

Constraints on Amendment Selection

One possible approach to the self-remediation of low-order detonation fragments is to amend the parent explosives with a reactive component whose activity would be triggered only by environmental exposure to sunlight and/or water. The environment of potential contaminant release is not known *a priori*, therefore, the ideal additives must be effective under a broad spectrum of conditions with respect to moisture, sunlight, ambient soil and water chemistry, and background biogeochemical processes on/in soils or surface waters. Neither the *types* nor the effective *dosages* of potential additives are established.

The most severe constraint, by far, on the design of self-remediation amendments is that it must have minimal impact on the performance, sensitivity, and shelf-life of munitions. Realistically, this constraint limits the volume fraction to a few percent for any amendment that does not contribute to the detonation energy. All of the amendments investigated here represent approximately 5 volume-percent or less; mass percentages are generally higher due to density contrasts. Given this stoichiometric imbalance, perhaps the most optimistic scenario for an amendment consumed in the target reaction would be for that additive to *initiate* the degradation and rely on subsequent environmental processes to complete the attenuation process. Amendments designed for catalytic or photocatalytic reactions would not be consumed, but may be constrained by transport of reactants to, or products from, the reactive surfaces. Of course, photocatalysts also require that sunlight reach the reactive surface, which may be problematic in soil environments where fine particulates, or reaction products, may occlude the surface.

General Considerations in Amendment Selection

A rational starting point in the selection of self-remediation amendments would be to adapt demonstrably successful remediation technologies for explosives, virtually all of which are applied at much more favorable, elevated reactant-to-explosive molar ratio (REMR). Many effective technologies have been developed for the treatment of explosives in: (1) dilute aqueous solution, as in groundwater plumes, and (2) crystalline form, dispersed in a soil matrix, as may be present in training target or impact areas, burn/disposal pits, or settling ponds at former packing or manufacturing plants. Of course, success at high REMRs is no guarantee of comparable success at the extremely low REMR required for explosives self-remediation.

The additives evaluated here were selected based on the following key criteria: (1) a documented ability to drive beneficial degradation reactions in explosives, (2) available as a powdered solid that is amenable to homogeneous dissemination throughout an explosives formulation, (3) chemically stable under atmospheric conditions, *e.g.*, not hygroscopic, (4) chemically compatible with explosives, binders, and other components prior to environmental or engineered wetting, and (5) not likely to introduce additional environmental or health risks.

Microbiological amendments are not considered due to three primary concerns: (1) the high concentrations of explosives is potentially inhibitory to growth, (2) biodegradation reactions are generally slower than abiotic reactions, and (3) possible misperception as biological weaponry.

Conversely, if these concerns are resolved, microbial amendments potentially could be self-sustaining.

Highly aggressive chemicals, such as strong bases, are not tested beyond a preliminary phase. Such amendments would require chemical isolation from the explosives and atmosphere, perhaps within a water-soluble encapsulation or by segregation into a chamber within the munitions casing.

As the first exploration of self-remediation additives for explosives, the present results serve to guide future development. The test formulations, particularly at the highest levels of amendment, are designed to elucidate potential self-remediation reactions, and in no way constitute a recommendation of a final design.

Alternatively, if low-levels of amendment can not affect sufficient self-remediation, then perhaps they can be useful in accelerating more traditional cleanup processes. For example, range clearing operations might be accelerated if the amendments can make explosives debris easier to locate for hot-spot treatment or for physical separation from the soil matrix.

Amendment Selections for This Study

Nitro reduction reactions are expected for explosives amended with either metal (Fe, FeNi) or sodium dithionite. Hydrolysis of explosives compounds is anticipated for formulations amended with an anatase photocatalyst. Only finely powdered, inorganic amendments are considered here so as to facilitate uniform dispersal within each formulation. Each of the amendment types are discussed more fully below.

Metallic Amendments. Aquifer restoration technologies involving granular or nanoparticulate, metallic iron – widely known as zero-valent iron (ZVI or Fe^0) – are well-established for the in-situ treatment of a variety of redox-sensitive contaminants. ZVI treatment may be a viable alternative for any contaminant for which its chemical reduction is deemed beneficial, including chlorinated solvents, hexavalent chromium, uranium, nitrate, and explosives (Tratnyek *et al.*, 2003; USEPA 2000).

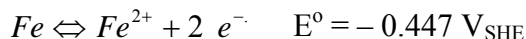
ZVI can rapidly and effectively drive the chemical reduction of explosive compounds, either directly at the metal surface or, more generally, in surface-catalyzed reactions with ferrous ions (Fe^{2+}) or microbial reactions supported by H_2 , both derived from Fe^0 corrosion (*e.g.*, Singh *et al.* 1999; Devlin *et al.*, 1998; Oh and Alvarez 2002; Nefso *et al.*, 2005; McGrath *et al.* 2000, 2001). The ZVI represents a substantial, but finite, reservoir of electrons to support nitro-reduction of explosive solutes. Complete reduction of all three nitro groups (R-NO_2) in TNT (R = aromatic ring) or RDX (R = the N-heterocyclic ring) may be neither achievable with such limited Fe^0 nor necessary. We hypothesize that only partial reduction of less than 100% of the explosives mass is necessary to generate more labile products that: (a) are more susceptible to natural attenuation in biologically active, organic-rich soils, and (b) may stimulate indigenous microbial activity by serving as a carbon source. Only the initial reactions proximal to the explosives material are considered here.

ZVI is readily available from multiple commercial vendors in a wide variety of particle sizes (*e.g.*, granular or powdered), compositions (pure or alloyed), and other relevant physical properties (*e.g.*, shape, specific surface area, internal porosity). These differences are reflected in a wide range of performance with respect to explosives degradation. A preliminary exploration several years ago identified powdered ZVIs that appeared to be much more

reactive than the granular or other powdered forms. Indeed, the powdered carbonyl iron reactive capacity was not exhausted by repeat challenges with fresh solutions of explosives, lasting much longer than other powdered irons (unpublished data).

In virtually all published reports describing reactions of explosive compounds with ZVI or Fe^{2+} , the explosive is an aqueous solute at concentrations well below its solubility limit. As a sparse amendment to munitions, the ZVI would be in intimate contact with dissolving, crystalline explosives. How ferrous ions would interact with *crystalline* explosives is unknown, but surface reactions may be significantly different at explosive concentrations that may be approaching their solubility limit proximal to the crystallite surface. It is conceivable that Fe^{2+} may bind covalently at the crystal surface or oxidize to Fe^{3+} and precipitate as an oxyhydroxide that may inhibit further dissolution. Inhibited dissolution could reduce the flux of explosive solutes to a level more manageable by natural attenuating processes. The weathered, mixed-valence iron oxyhydroxides also will serve as a catalyst for continued chemical reduction and adsorption, so long as Fe^{2+} is available (Nefso *et al.* 2005). Conversely, it is also possible that the explosive solutes may overwhelm and passivate the iron surfaces; the immobility of oxidized ferric iron (Fe^{3+} or $\text{Fe}[\text{III}]$) in oxyhydroxides may make this scenario more likely.

Powdered Iron-Nickel. A powdered iron-nickel alloy (4Fe:1Ni) is evaluated here, only in the PBXN formulation, for comparison with the pure iron amendment. This test is intended to evaluate the hypothesis that the Galvanic corrosion induced by the introduction of a more noble metal to the iron will accelerate the oxidation of iron to Fe^{2+} and, thereby enhance the chemical reduction of explosives. Standard oxidation-reduction or half-cell potentials for relevant Fe and Ni reactions include the following:



Note that the potential of the Ni oxidation reaction is ~0.2 V less negative than that for Fe oxidation (Jones 1996). Although the principles of Galvanic corrosion are well established, no studies have tried to take advantage of the process to accelerate explosives treatment with bimetallic alloys.

Powdered Anatase. Titanium dioxide (TiO_2) is well documented as a photocatalyst (Diebold 2003, Braun *et al.* 2010), most effective under UV radiation ($\lambda = 10\text{-}400$ nm, with energies of 124-3 eV, respectively). TiO_2 forms three crystalline polymorphs that are highly stable under environmental conditions: rutile, anatase, and brookite. Differences in crystal structure are reflected in differences in the photochemical behavior of these semiconductors (*e.g.*, band gap). Anatase is generally considered the superior photocatalyst. TiO_2 minerals are very stable and pose no environmental or health risk in soils or aqueous environments as a chemical or particulate. TiO_2 photocatalysts are commercially available or can be prepared in the laboratory by sol-gel methods.

TNT and associated nitroaromatics in aqueous solution can photodegrade in sunlight. Phototransformation commonly involves oxidation of methyl groups, reduction of nitro groups, and dimer formation. These reactions generate nitrobenzenes (*e.g.*, 1,3,5-trinitrobenzene, TNB), benzaldehydes, azoxydicarboxylic acids, and nitrophenols (Spanggord *et al.* 1980, Mabey *et al.* 1983, Layton *et al.* 1987, Son *et al.* 2004, Makarova *et al.* 2000). Heterocyclic nitroamines, such as RDX and HMX, are also susceptible to photolysis. RDX phototransformation products tend to be of lower molecular mass and include ammonia, formaldehyde, nitrate and nitrite, nitrous

oxide, and N-nitroso-methylenediamine (Glover and Hoffsommer 1979; McCormick *et al.* 1981).

Few studies have been conducted to evaluate photodegradation processes and products at the surface of crystalline explosives, although it has long been known that explosives fragments containing TNT will weather in the environment to a reddish brown color. Pennington *et al.* (2007; SERDP CP-1155) report very limited photodegradation of TNT or RDX associated with either pure or mixed (Comp-B) crystalline surfaces (unamended formulations). As anticipated, much faster rates of photodegradation were observed for dissolved TNT and, to a lesser degree, RDX. These experiments were conducted in sealed vessels under a light source measured in the UV-A range ($\lambda = 320\text{-}390\text{ nm}$) between 0.02 and $0.0023\text{ mW}\cdot\text{cm}^2$ and between 2.7 and $0.3\text{ mW}\cdot\text{cm}^2$ over a broader spectrum ($\lambda = 305\text{-}2800\text{ nm}$). The ranges in irradiance reflect exposure of samples at 3 different distances from the light source. This UV irradiance is one to two orders of magnitude lower than employed here or than is present in natural sunlight, as measured in Vicksburg, MS.

Chio *et al.* (2006) report that dissolved RDX and HMX photodegraded with pseudo-first-order kinetics on UV-irradiated TiO_2 , with reaction products that included NO_3^- , NO_2^- , NH_4^+ , and formate as a transient intermediate. For both nitroamines, photocatalysis was very effective, while, individually, UV radiation or TiO_2 affected little change. The same group of investigators had previously reported similar results for UV photocatalysis of TNT on TiO_2 (Son *et al.* 2004), although dissolved TNT was more susceptible to UV-only photodegradation. The irradiance for these experiments was much greater than employed here – $4.2\text{ mW}\cdot\text{cm}^{-2}$ at 15 mm from the source bulbs, measured at 245 nm (in UV-C range), with exposure along the entire 0.5 m flow path.

Doped Anatase Photocatalyst. Any self-remediation amendment utilizing photocatalysis must rely exclusively on solar insolation, which imposes certain limitations. The intensity of solar insolation varies diurnally and seasonally, as well as with latitude and climate. The spectrum of sunlight at the earth surface is dominated by the visible spectrum (750-380 nm; 1.6-3.27 eV), with very limited UV-A radiation ($\lambda = 400\text{-}315\text{ nm}$; 3.10-3.94 eV) and still less UV-B radiation ($\lambda = 315\text{-}280\text{ nm}$; 3.94-4.43 eV) (ASTM reference spectrum; Emery 2003). Natural UV radiation may not provide sufficient energy to drive substantial photocatalysis of explosives on unmodified TiO_2 , which absorbs primarily in the UV range (Diebold 2003). However, the photocatalytic properties of TiO_2 can be modified by adding various dopants which serve to expand the range of light energy adsorbed into the visible part of the spectrum.

Photocatalyst development is an extremely active area of research with respect to both substrate and dopant. The selection of an anatase-based photocatalyst is largely due to its established dominance and chemical stability (Diebold 2003). Tungsten trioxide (WO_3) is one of many dopants known to expand the absorption range of TiO_2 into the visible spectrum (Song *et al.* 2006; Chai *et al.* 2006, Lorret *et al.* 2008). Doped TiO_2 can be prepared in the laboratory, but the powdered, WO_3 -doped anatase used here was one of very few that was available commercially.

Photocatalytic self-remediation requires that light reach the TiO_2 surface. If the surface is buried or occluded by soil components (*e.g.*, clays, microbes) or insoluble munitions residue, the effectiveness of the photocatalyst may be impaired.

Na-Dithionite. Dithionite is a chemical reducing agent that has been demonstrated in field-scale remediation, although not in the fashion explored here. Like ZVI, dithionite can be used to create a zone of low electrochemical potential within the path of redox-sensitive contaminant plumes. However, to date, dithionite has been used to create treatment zones by chemically reducing ambient, immobile iron to the ferrous form, which then serves to reduce target solutes in the passing plume of chlorinated solvents (Fruchter *et al.* 2000). This reduction zone method conceivably could work for explosives plumes as well.

Powdered dithionite as a self-remediation amendment was not part of the original or limited-scope proposals for this study. Dithionite is considered only in the supplemental, Comp-B evaluation.

Potential Environmental Impact of the Amendments. The environmental fate any amendments must be considered, independent of the munitions detonation completeness. Amendments in low-order detonation fragments ideally would be consumed if they are directly involved in the self-remediation reactions. The same amendments in a fully detonated material also would be consumed or rendered benign. Potential release of amendments from fully detonated material is not evaluated experimentally here. At the current formative level of self-remediation technology development, far from any fieldable technology, consideration of amendment fate is an important secondary concern to be anticipated. When promising technologies are identified, these potential environmental effects must be revisited.

The powdered iron amendment is unlikely to present any significant environmental risk because, regardless of detonation history, rapid oxidation is expected to form benign oxyhydroxide phases already common in natural soils. Similarly, the anatase amendment does not present an environmental risk due to its effectively inert nature. The dithionite amendment is expected to react with reducible soil components to yield benign sulfate species. Eventual corrosion of the more noble nickel in the iron-nickel amendment may pose an environmental risk once the metallic iron is oxidized. If the Galvanic corrosion approach shows promise, alternative metals could be considered for the relatively noble component. Experiment leachates are analyzed only for explosives.

Important Aspects Deferred to Future Investigations

Promising approaches to self-remediation must be defined before they can be refined. The handful of amendments evaluated here represents only an exploration of potential, self-remediation mechanisms. It is unlikely that these first attempts will identify a field-ready technology. Some approaches may show promise, while others will appear to fail. The limited scope of this study does not permit more than conjecture as to *why* any particular amendment did or did not meet expectations. This investigation may be considered successful if it stimulates thought or informs future efforts toward the fielding of self-remediation technologies for explosives.

Several critical aspects in the full development of a self-remediation technology are beyond the scope of this investigation, including the following: (1) attenuation processes outside the immediate domain of the explosives, (2) potential environmental risks associated with amendments or reaction products, (3) shelf-life of amended munitions, and (4) amendment effects on detonation performance.

Successful self-remediation technologies will likely require a strategic coupling of engineered and natural processes. One of the deferred working hypotheses for this investigation is that explosives-degrading, environmental, biogeochemical processes will be enhanced by the transformations *initiated* in the self-remediation reactions. A related hypothesis is that the initial self-remediation products are more labile and will promote growth of explosives-degrading soil microbes within the “microplume” environment proximal to an amended explosives fragment. Increased biomass in key microbial populations could further enhance the natural attenuation processes. Irreversible binding of amino derivatives to soil organics also could be enhanced. Other potentially important environmental variables are not considered here, *e.g.*, soil composition and field-like cycles of moisture, light, and temperature, are aspects that should be addressed in any expanded investigation.

Only individual, abiotic amendments are explored here. Future evaluation could consider biotic amendments and combinations of amendments, *e.g.*, a synergistic combination of chemical, photochemical, and biochemical additives.

Potential health or environmental risks associated with the amendments themselves or reaction products will certainly be a concern for any fielded technology. Other than avoiding highly toxic additives, amendment-associated risk is a secondary consideration at the current primitive state of development. Metal concentrations in the leachate (*e.g.*, Fe, Ni, W, Ti) are not monitored in the present investigation, but may be an important concern in future investigations.

Demonstrations of long-term chemical stability of amendments and amended formulations in storage, as well as their undiminished detonation performance, would require an extended study under a variety of conditions. Such studies are premature until effective self-remediation amendments are demonstrated.

METHODS & MATERIALS

Materials

Two explosives formulations are considered here. The PBXN-107 was prepared at ARDEC using stock RDX material. The PBXN-107 components detailed in Table 1 were procured from the sources indicated. Flaked Comp-B was obtained from Holston Army Ammunition Plant and reformulated with amendments at ERDC-Vicksburg.

Four inorganic amendments are evaluated for self-remediation potential. The PBXN-107 was amended with carbonyl iron, carbonyl iron-nickel, and WO_3 -doped anatase TiO_2 . The Comp-B was amended with the same carbonyl iron and anatase, as well as with powdered sodium dithionite. The carbonyl iron is a MICROPOWDER[®] Iron R-1470 (1140060 Lot # 6082232) from International Specialty Products (ISP), Wayne, NJ, USA. The carbonyl iron-nickel alloy is FLOWMASTER[™] Metal Powder Carbonyl Iron with 20% Nickel (tribochemically alloyed); 325 mesh particle size (Lot 2035; 26.28(20)325). The anatase is FLOWMASTER[™] Oxide Powder Titanium Dioxide, doped with 3 wt% WO_3 ; 325 mesh particle size; Lot 6021 (22.8/325). Laboratory grade, powdered, sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$; sodium hydrosulfite) was obtained from Fisher Scientific.

Methods

The overall approach involves the systematic preparation and testing of a suite of munitions formulations containing alternative inorganic amendments at low volume fractions ($\leq 5\%$). Below are brief descriptions of methods employed for the following tasks: (1) preparation of PBXN samples, (2) preparation of Comp-B samples, (3) safety testing of the PBXN, and (4) self-remediation experiments.

PBXN Preparations. Multiple concentrations of the metal or oxide additives were mixed into standard PBXN-107 formulations at the U.S. Army Armament Research, Development and Engineering Center (ARDEC), Picatinny, New Jersey. Preparations yielded replicate tablets containing 0, 5, 10, and 15 weight-% of three separate additives described previously – Fe, FeNi (4Fe:1Ni), and doped anatase.

Briefly, PBXN sample preparation for this study involved blending an acrylic binder gel, mixing in the RDX and any self-remediation amendment, pressing the mixture into a thin sheet, extended curing under heated vacuum, then press-cutting sample tablets. Each of these major steps is depicted in [Figure 1](#). Forming a PBXN formulation into sheet is not standard practice, but is designed to produce small uniform tablets for evaluation in the self-remediation column experiments.

Each master-batch of binder is prepared by weighing out all the liquid ingredients (1-4 in Table 1) into a beaker, except for the tert-butyl peroxybenzoate (TBPB). The cobalt compound is added to the beaker. The Aerosil silica is weighed out, added to the liquid ingredients, and mixed with the homogenizer until a smooth gel is formed (upper right in [Figure 1](#)). Quantities sufficient only for immediate use are prepared, *i.e.*, only fresh mixtures are utilized.

Powdered RDX is mixed with 3.3 ± 0.2 weight-% DOM (Triethylene glycol dimethacrylate) to form a mixture referred to as CXM-3. Each formulation will consist predominantly of CXM-3, with lesser amounts of master-batch binder mix and tert-butyl peroxybenzoate in proportions

indicated in Table 2. PBXN-107 formulations were prepared to yield the prescribed 86% RDX and 14% binder. The unamended PBXN-107 batch was prepared first, followed by individual amendment series preparations, cleaning the equipment between amendments.

Self-remediation amendments were added at the 5, 10, or 15 weight-% levels with the mass of the other components reduced proportionally (see Table 2). The ratio of non-amendment components remains consistent across all formulations. The ratio of acrylic binder to crystalline solids (primarily the RDX and amendments) will deviate slightly from the unamended formulation due to differences in amendment particle density.

All beakers containing the unique mixtures are placed into a nitrogen-atmosphere glove-box and re-flushed with nitrogen. Requisite equipment and tools – a mortar and pestle, Teflon molds, and Teflon spatulas – are prepositioned in the glove-box. Each formulation is mixed in a mortar for 10 minutes before being pressed into molds and spread evenly. Molds are removed from the glove-box and immediately placed in a vacuum oven at 40°C for seven days, monitoring and maintaining the vacuum as necessary.

At the end of the 7-day curing process, the molds are removed from the vacuum oven. Disk-shaped samples are cut from the sheet with a cork punch. At least 6 disks with a nominal diameter of 1.6 cm are produced for each of the amended formulations; at least 9 disks of the unamended formulation are prepared. Samples were shipped securely to ERDC in Vicksburg, MS.



Figure 1. Major, sequential steps (clockwise) in the preparation of PBXN-107 samples, starting with binder preparation in the top center image, mixed to a gel, mixing in RDX w/wo amendments (lower right), pressing into a sheet under N_2 atmosphere (glove-box), which is cured at 40 °C under vacuum for 7 days before cutting disks of ~0.5 g for self-remediation and sensitivity testing.

Table 1. Summary of components in PBXN-107 binder (#1-#6)		
Abbreviation	Compound	Wt% in Binder Mix
1. EHA	2-Ethylhexyl-acrylate, 98%	50.16
2. NVP	1-vinyl-2-pyrrolidinone, 99+%	33.74
3. DOM	Triethylene-glycol-dimethacrylate, 95%	8.97
4. TGDM	Bis-2-ethylhexyl-maleate, 90%	0.66
5. Silica	Aerosil® R972	6.38
6. CoAA	Cobalt [II] Acetylacetonate, 99%	0.09
		SUM = 100
TBPB	Tert-butyl peroxybenzonate, 98%	
CXM-3	RDX and 3.3± 0.2 % DOM	
All compounds from Aldrich except the Silica from Evonik Degussa		

Table 2. Component mass (grams) for 25 gram batch of each formulation				
Ingredient	Unamended	5% Additive	10% Additive	15% Additive
CXM-3	22.234	21.121	20.011	18.899
Binder Mix	2.7415	2.604	2.467	2.330
TBPB	0.025	0.024	0.023	0.021
Total:	25.0005	25.000	25.000	25.000

Preparation of the unamended samples was largely successfully (Figure 2A). Samples were pliable and remained intact during self-remediation experiments. A minor degree of heterogeneity was evident in the contrasting appearance between the smooth bottoms (facing Teflon mold) and rough tops (exposed to open vacuum).

Unfortunately, each of the 3 amendments appears to interfere with the curing process to varying degrees, generally in proportion to the weight fraction added. The TiO₂-amended samples (Figure 2B) remained largely intact but friable at the 5% amendment level, but the 10% and 15% samples were highly friable. The Fe-amended samples (Figure 2C) were somewhat sticky on one side (facing Teflon mold) and friable on the exposed side. Higher amendment levels further exacerbated the problem. All of the FeNi-amended samples (Figure 2D) were highly friable.

Scanning Electron Microscope (SEM) examinations of the PBXN materials (Figure 3) are encouraging for two reasons: (1) a reasonably uniform distribution of the amendments is evident, and (2) the amendments appear to be exposed, *i.e.*, not occluded by acrylic binder. Figure 4 reveals the morphology of the carbonyl Fe amendment in pure sample.

The compromised physical condition (and possibly chemical condition) of the PBXN samples precludes meaningful, quantitative comparison of self-remediation results within and between treatments. The degree of RDX crystallite exposure to the aqueous phase is highly variable but generally proportional to the level of additive present. Nevertheless, the sensitivity and self-remediation potential of these formulations were conducted with the intent of detecting some trends in degradation processes.

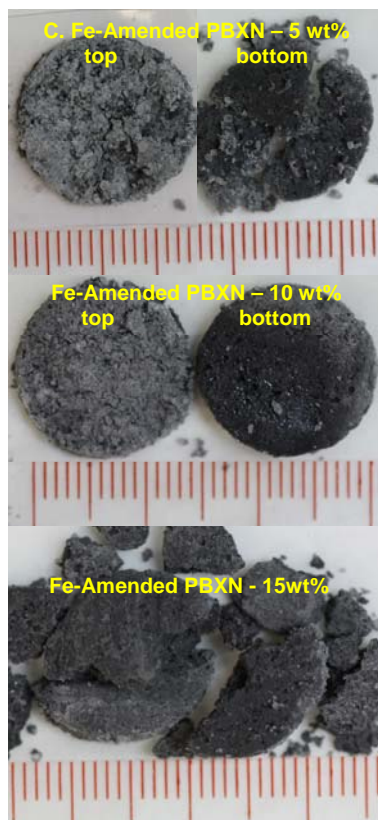
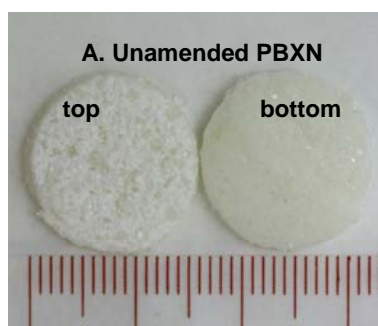
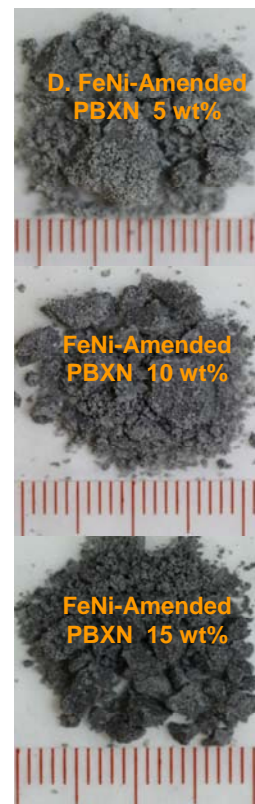


Figure 2. Photographs of PBXN-107 preparations: (A) unamended; (B) TiO_2 -amended; (C) Fe-amended, and (D) FeNi-amended. Note heterogeneity in all samples and the friable nature in all amended samples except the 5%- TiO_2 .

Scale: 1 mm divisions on ruler; nominal sample disk diameters are 15-16 mm.



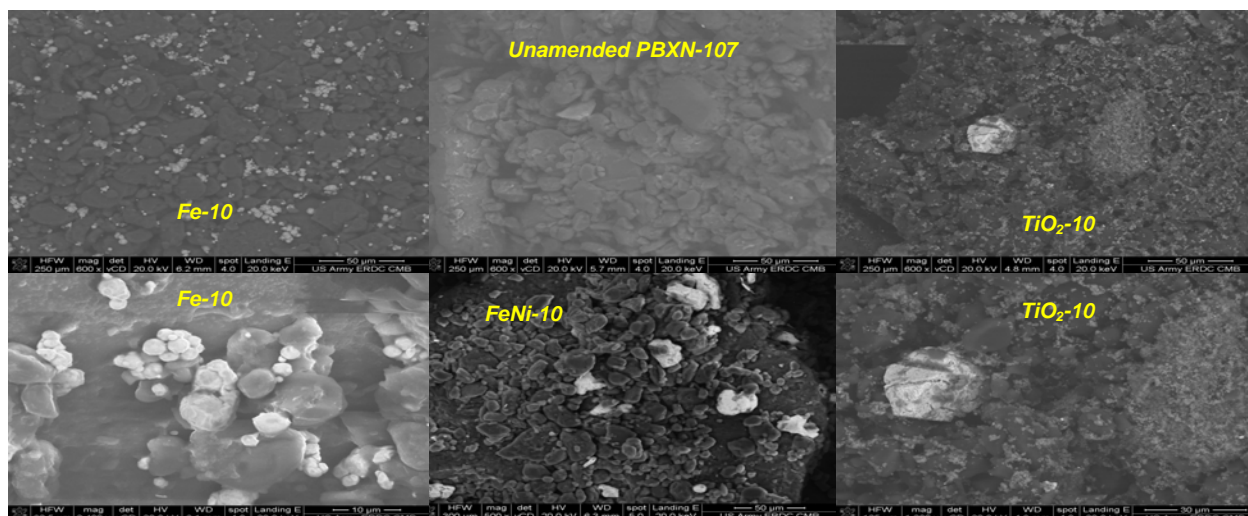


Figure 3. SEM images of PBXN-107 unamended (top, center), amended with Fe (left), amended with FeNi (bottom, center), and amended with TiO_2 (right). Note that the amendments, which appear brighter in the images, are well distributed within the mixture.

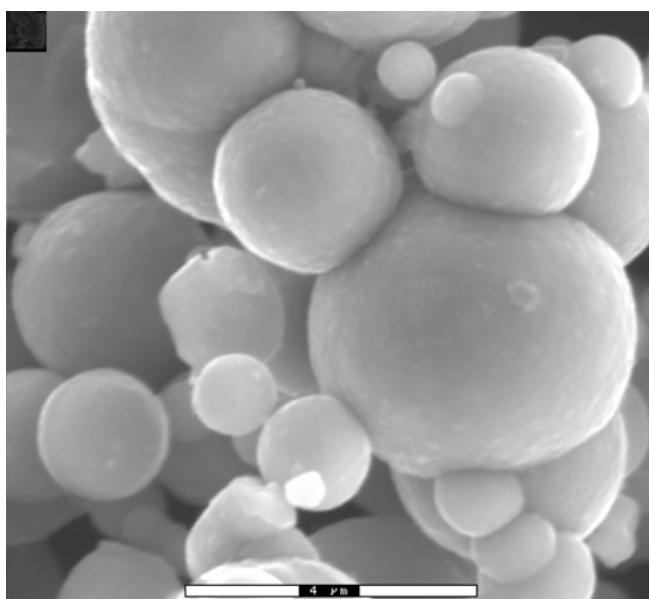


Figure 4. SEM image of powdered carbonyl iron, which previous batch experiments revealed to be exceptionally effective at explosives solute transformation.

Scale bar: 4 microns (μm).

Imaged at 10,000x by C. Weiss & C. McGrath, ERDC-Vicksburg

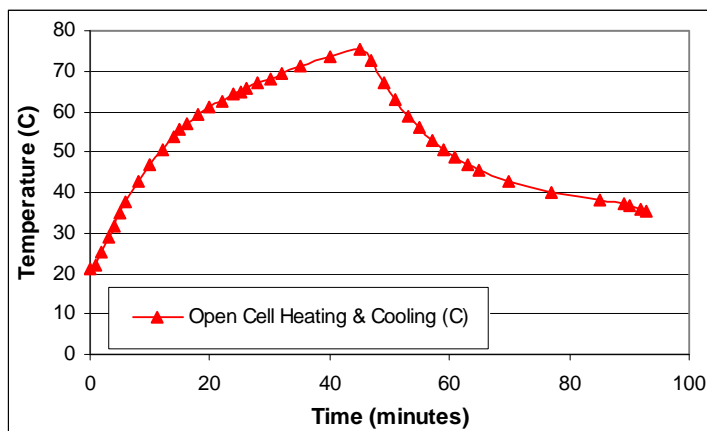
Composition B Preparations. The Composition B formulations were prepared by amending an existing Composition B with 5 volume-percent of additives. Flaked Composition B was crushed to a fine powder in a mortar and pestle until no large grains were visible. The pale yellow or off-white color of the uncrushed material is readily distinguishable from the white crushed material. Enough material was crushed to prepare the entirety of any particular amendment suite, starting with the unamended material.

Each sample tablet was prepared individually. Approximately 0.50 g of crushed material and an appropriate mass of amendment to achieve 5 vol-% were weighed out (see Table 3). Any amendment was mixed extensively with a small spatula for at least 5 minutes and well beyond the physical appearance of homogeneous mixing. The uniform volume-% approach generates a nearly uniform amount of explosives in each replicate with the intent of approaching sample size uniformity and facilitating direct comparison of self-remediation performance.

All preparations, including the unamended samples, were prepared by recasting the crushed and mixed material under pressure and heat. The mixed powders were poured into a 13 mm, stainless steel die (Specac) between two, polished, stainless steel disks, and pressure-sintered into uniform tablets (press assemblage is in the Figure 5 foreground). Between 2000-4000 psi pressure was applied to the die while being heated externally by two, 250 watt, heat lamps placed on either side at a distance of approximately 3 inches; the apparatus is shown in Figure 5. Temperature within the die was not monitored during sample pressing. However, the heating and cooling trends are approximated by the plot in the Figure 5, which depicts the changes in temperature within an open die (atmospheric pressure), packed with quartz sand and a Hg thermometer, under identical heating conditions. Hydraulic pressure between 2000 and 4000 psi was applied to the die for 20 minutes using a SpectoPress, and maintained manually to



Figure 5. (A) Apparatus for the preparation of all Composition B tablets. Powdered mixtures were placed in a 13 mm, stainless steel die (in foreground; Specac Model 3000) and subjected to elevated pressure (3000 to 4000 psi) using the SpectroPress for 30 minutes. The die, initially at room temperature, was heated externally using dual, 250-watt, heat lamps, placed ~3 inches away on either side. (B) Temperature trend monitored during the heating and partial cooling in an open, sand-packed die.



compensate for pressure reduction arising from sample compaction and very minor seepage of material between metal parts. The internal temperature at 20 minute would be approaching 60 °C, well below melting temperatures of TNT (~80.4 C) or RDX at (205.5 C) at 1 atm pressure. The heat lamps were removed and samples allowed to cool at the elevated pressures for 5 minutes, then pressure was allowed to drift downward as cooling continued for 5-10 minutes. Tablets were removed from the die, wrapped in foil, and placed in sealed plastic bags for no more than 10 days when self-remediation experiments were initiated.

The pressure-sintering approach yielded test samples of similar size, mass (Table 3), and physical integrity (see leftmost tablets shown in Figures 15 and 20 in the Results section). The Comp-B samples remained intact throughout all self-remediation tests.

Table 3. Summary of Composition B preparations with 5 vol-% amendments				
Sample		Comp B Mass ² (g)	Amendment Mass ³ (g)	Initial Tablet Mass ⁴
Unamended ¹	B-A	0.5016	—	0.4917
	B-B	0.5001	—	0.4880
	B-C	0.5008	—	0.4923
	Avg±Std.Dev:			0.4907 ± 0.0023 (3)
	TB-A	0.5029	—	0.4965
	TB-B	0.5009	—	0.4957
	TB-C	0.5009	—	0.4968
	Avg±Std.Dev:	0.5012 ± 0.0110 (n=6)		0.4963 ± 0.0006 (3)
Fe-Amended	Fe-1	0.5009	0.1063	0.5900
	Fe-2	0.5007	0.1064	0.5915
	Fe-3	0.5003	0.1063	0.5921
	Avg±Std.Dev:	0.5006 ± 0.0003	0.1063 ± 0.0001 (17.5 wt%)	0.5912 ± 0.0011
TiO ₂ -Amended	Ti-1	0.5004	0.0608	0.5563
	Ti-2	0.5006	0.0608	0.5557
	Ti-3	0.5005	0.0608	0.5561
	Avg±Std.Dev	0.5005 ± 0.0001	0.0608 ± 0.0000 (10.8 wt%)	0.5560 ± 0.0003
Dithionite-Amended	Di-1	0.5001	0.0339	0.5233
	Di-2	0.5007	0.0337	0.5237
	Di-3	0.5004	0.0338	0.5258
	Avg±Std.Dev	0.5004 ± 0.0003	0.0338 ± 0.0001 (6.3 wt%)	0.5243 ± 0.0013
¹ Two unamended suites: B-A to -C for the dark experiments; TB-A to -C for the lighted experiments. ² Mass Comp-B powder into preparation, or post-pressing mass for unamended tablets (minor losses in sintering) ³ Mass of 5 vol-% amendment ⁴ Mass of tablet used, after surface roughening on both sides (dark experiments) or top side (lighted experiments)				

All surfaces of the Comp-B tablets appeared very smooth and shiny due to contact with the polished metal surfaces in the die. However, accumulation of wax binder at the edges might also have been a factor. In order to present a sample that might be more representative of a low-order

detonation fragment, the sample surfaces were uniformly roughened by minimal scuffing with very fine sand paper (320 grit). Both sides of the metal- or dithionite-amended suites were roughened; only the exposed top surfaces of the TiO_2 -amended suites were roughened. Loose material was dusted off gently with a jet of compressed air.

Safe handling of explosive material is essential. A grounding wire was worn to minimize buildup of potentially hazardous static electricity when mixing powdered material. A full face shield or safety goggles was worn while handling powdered material. No detonation or deflagration incidents occurred. Both ARDEC and ERDC had recently revised safety protocols for handling explosives material.

PBXN Sensitivity Testing

Samples of neat and amended formulations were subjected to a suite of sensitivity tests. Assessments of additive stability in the PBXN mixture are required to assure safe handling during preparation, shipment, and subsequent environmental testing.

Impact Sensitivity Tests. Impact Tests were performed on all of the PBXN-107 formulations, tested “as-is”. The ERL, Type 12 impact tester, utilizing a 2.5 kg dropweight, was used to determine the impact sensitivity of each sample. The drop height corresponding to the 50% probability of initiation is used to measure impact sensitivity. The ERL, Type 12 Impact Test Method is described in STANAG 4489 Ed.1 "Explosives, Impact Sensitivity Tests".

BAM Friction Test. The BAM large friction tester was used to determine the friction sensitivity of the sample. Approximately 30 mg of sample was placed on the porcelain plate. The porcelain pin was lowered onto the sample and a weight was placed on the arm to produce the desired load. The tester was activated and the porcelain plate was reciprocated once to and fro. The results are observed as either a reaction (*i.e.* flash, smoke, and/or audible report) or no reaction. Testing is begun at the maximum load of the apparatus (360 N) or lower if experience warrants such. If a reaction occurs in ten trials, the load is reduced until no reactions are observed in ten trials.

The ABL Friction Test Method. The unamended PBXN-107 was too coarse to test on the BAM Large Friction apparatus. The ABL test friction was conducted instead. The *ABL Friction Test Method* is detailed in the Department of Defense Explosives Hazard Classification Procedures, ARMY TB 700-2 dated 5 January 1998. It is also described in MIL-STD-1751A, dated 11 December 2001, Method 1021, “Friction Sensitivity – ABL Sliding Friction Test”. The sample is subjected to vertical compression force under a non-rotating wheel, while the sample is moved in a horizontal direction on a sliding anvil. A sample is placed on the anvil, under the wheel, in a thin uniform layer (equivalent to one particle thickness for solids based on largest particle size in distribution). The wheel is lowered onto the sample and force is applied to the wheel. An initial pressure of 1,000 psi is typical. Values of 1,800 psi maximum to 10 psi minimum are used. A pendulum impacting on the edge of the anvil propels the anvil at a known velocity, perpendicular to the compressive force that is applied to the sample. An iterative procedure is used to determine the highest compressive force at which no positive results are obtained in 20 trials. This value is considered the Threshold of Initiation (TIL). A trial is considered positive if any of the following results is obtained: (a) visible sparks; (b) visible flames; (3) audible explosion, (4) loud crackling noise, (5) detection of reaction products by a gas analyzer.

Electrostatic Sensitivity Test. The Electrostatic Sensitivity Test is described in MIL-STD-1751A, dated 11 December 2001, Method 1032, "Electrostatic Discharge Sensitivity Test (ARDEC [Picatinny Arsenal] Method)". Reaction indicators, as described above, are recorded for 20 trials applying a 0.25 J charge, which is the maximum energy level of test apparatus.

Detonation Velocity Assessment. Detonation velocities for the various PBXN mixtures were not measured directly in this preliminary phase of this investigation. However, detonation velocities and other important characteristics can be estimated with the CHEETAH thermochemical model, v.5.0 (Bastea *et al.* 2007).

Self-Remediation Column Experiment Design

The self-remediation experiments are the central focus of this exploratory investigation. In brief, crystalline explosive samples of known initial mass and composition were placed on or within a short column of packed sand and flushed intermittently with a uniform amount of deionized water. Columns were kept either in a dark or lighted, closed chamber between wetting events. Gravity drainage was captured in an amber glass vial over several days and analyzed for explosives by HPLC.

There were no previous investigations of explosives self-remediation to guide this pioneering investigation, and certainly no standard procedures. Thus, minor interim adjustments to experimental conditions or procedures were made during the course of these experiments. However, columns within any particular experimental suite experienced the *same* conditions and treatments. The Comp-B experiments benefited from lessons learned in the PBXN evaluations; likewise, these investigations will inform future experimental designs.

The nature and amount of self-remediation amendments are the primary experimental variables. Important environmental conditions – water flux, light exposure, and temperature – were uniformly applied to any particular suite of preparations. Monitoring on at least a daily basis documented variation to be within narrow ranges. Where conditions are otherwise uniform, comparisons can also be made between experimental suites.

Column Construction. Each of the packed columns consisted of a 12 mL (graduated), polypropylene, Whatman syringless filter with an inner diameter of 2 cm and full internal height of 5 cm (Figure 6). Effluent passes through a 0.45 μm , glass microfiber (GMF) filter into a luer slip which is inserted into a hole drilled in the collection vial cap. The entire column fits securely around the vertically-ribbed cap of the 20 or 40 mL, amber glass vials used to collect effluent. To prevent any pressure buildup within in the collection vial, a thin, deep, vertical cut was made in the cap corner. The luer-cap seal is very tight due to the rubber liner inside the cap; the tiny cut allows for pressure equilibration between the otherwise sealed vial and the atmosphere. The amber vials minimize potential for photodegradation of dissolved explosives after exiting the columns.

A uniform, coarse-grained ($\frac{1}{2}$ -1 mm nominal diameter), quartz sand served as the porous medium in the columns. The sand was washed in 10% HCl and rinsed with deionized water so as to minimize potential microbial activity and keep the focus on dissolution and abiotic reaction processes. No additional precautions were taken to prevent microbial activity. It is unlikely that explosives-degrading microbes could enter these controlled laboratory systems via airborne pathways. However, subsequent research should utilize natural, biologically active soils, preferably from an active training range, and monitor any critical changes in microbial biomass or metabolism.

Sample suites used to assess the Fe, FeNi, or dithionite amendments were buried within the packed columns at approximately $\frac{2}{3}$ of the column height, *i.e.*, near the 8 mL level. These samples were expected to remain wet at all times with only indirect air contact and negligible opportunity for photodegradation. Of course, all samples used to assess photocatalytic effects of the TiO₂ amendments had to be placed at the top of the packed columns to permit exposure to light.

Each additive (Fe, FeNi, TiO₂, dithionite) and concentration level was evaluated in triplicate columns. The Fe-amended PBXN columns were run first at the 5, 10, and 15 weight-% amendment levels. Next, the TiO₂ and FeNi amended PBXN suites were evaluated. In light of the Fe-PBXN results and compromised condition of the FeNi samples, only the 10 and 15 wt-% FeNi were evaluated. Finally, as a supplemental study, the Comp-B suites containing a uniform 5 volume-% of each amendment was considered. Unamended samples accompanied each of the amended suites in triplicate or duplicate (two separate pairs).

Intermittent Wetting. Some level of exposure to water is an essential component in all of the self-remediation approaches considered here. The presence of liquid water is a convenient indicator of environmental exposure that can serve as a trigger for self-remediation.

The initially dry columns were wetted gradually, generally by introducing 5 mL of deionized water to the lower edge of an inclined column for at least the first day. The purpose of the gradual, asymmetric wetting was to minimize air entrapment. Trapping some air would not be problematic for the task at hand, but uniformity between columns was a goal. Subsequent wetting events involved the gentle, dropwise release of 1.0 to 2.0 mL of deionized water (18 Ω) to the top of the sand. For the TiO₂ suites, water was applied directly to the explosives material. Infiltration was rapid, though water would bead briefly on the intact TiO₂-amended Comp-B tablets.

An intermittent wetting scheme was selected because: (1) it could be applied uniformly within and between test suites, (2) although synthetic, it approximates natural cycles more closely than do alternatives such as continuous flushing, and (3) dissolution of munitions explosives is a very slow process, so extended periods between wetting events would permit systems to approach equilibrium, at least proximal to the reactive interfaces.

The Fe-amended PBXN suite of columns (3 of each Fe content and 2 unamended replicates) were initially wetted with 5 mL, followed by twice daily applications of 2 mL – morning (7-10 AM) and evening (5-8 PM), without interruption. After 17 days (5 samples) of flushing, the columns were slowly dried out to assess mass loss from explosives dissolution. Wetting was resumed for another 13 days (5 samples), though drainage was noticeably slower.

The FeNi-amended PBXN suite (3 of each FeNi and 2 more unamended replicates) received 5 mL of initial wetting, followed by 2 mL applications, twice per day, for 34 days. A total of 11 effluent samples were collected, each representing a period of 3 days (4 for the initial sample).

The TiO₂-amended PBXN suite (3 of each TiO₂ and 3 unamended replicates) also received an initial 5 mL wetting, followed by two 1 mL treatments per day. Sample collection intervals were extended to 4 days (5 for the initial sample) due to reduced breakthrough volume, presumably due to evaporative losses at the elevated temperatures (22-32 °C vs. 17-19 °C in the dark experiments). Wetting volumes were increased to 1.5 mL for days 19 to 35 to boost effluent volumes slightly. A total of 9 samples were collected for analysis.

Comp-B amended with Fe or dithionite and associated blanks (both in triplicate) received 2 mL on the first day, then 2 mL twice per day until day-17 (7 samples). TiO₂-amended Comp-B and unamended replicates were wetted with two 2 mL applications on the first day to approach column saturation very slowly, then with dual 1.5 mL wettings for the first 3 days. The wetting volume was increased to 2 mL twice daily for days 4 to 26 to enhance column flushing and

increase the minimum effluent volume. Six samples were collected, each representing a time interval of 4-5 days.

Light Sources and Monitoring.

The TiO₂ photocatalyst amendments were tested in a small light chamber. The chamber was constructed of plywood with interior dimensions of 50.5 cm width, 20.5 cm depth, and a working height of 52 cm (below light fixture; 63 cm total height). Interior surfaces were spray-painted with high-gloss silver enamel. Vertical position of the samples within the chamber was adjusted using blocks or sheets of foam rubber. A beaker of deionized water was placed at each end of the tray supporting the columns in order to raise internal humidity and minimize evaporation of column water. Water temperature in one of the beakers was measured at least daily, immediately upon opening the chamber for wetting events, and taken to represent trends in steady-state thermal equilibrium within the chamber.

The light source held two, 18-inch, fluorescent bulbs. The bulb types were changed toward higher energy radiation over the course of the experiments in order to identify requisite conditions for photodegradation if little had been observed at the lower energies. Initially, one bulb was UV-A (General Electric, F15T8/BLB; 15 watt) and the second was a broad-spectrum bulb for plant growth (General Electric, F15T8/PL/AQ; 15 watt). On day-13 of the PBXN-Fe experiment (starting with 4th sample) the light source was changed to two UV-A bulbs and remained as such through the rest of the PBXN experiments. The Comp-B experiments started with two UV-A source lamps. Seeing only small indications of photodegradation products in the effluent, one of the bulbs was replaced with a UV-B bulb [UVP Inc. (Upland, CA) F15T8.UV-B; 15 watt] on day-16.

Columns were secured beneath the light source within a perforated foam-rubber base. Column placement was in a zig-zag pattern as close as possible to the central axis of the light source and its midpoint. Column positions were altered each day by reversing orientation of the base in order to minimize any differences attributable to contrasts in the light sources. Column positions in the base holder were rearranged whenever fresh sample collection vials were installed.

Initially, the PBXN samples were placed 38.3 cm from the light source. Seeing no indication of transformation products in the effluent, the samples were raised to 23.5 cm from the light on day-8. Again, on day-12 the samples were raised to 7.5 cm from the light source. This distance was maintained for the remainder of the PBXN experiment and the entire Comp-B experiment.

Light irradiance was measured at least daily at the same elevation as the explosives samples, generally in conjunction with the morning wetting events. Two wavelength ranges were measured: UV-A and wide spectrum. A PMA2100 photometer and PMA2141 Pyranometer (Solar Light Co., Glenside, PA) measured the broad spectrum (305-2800 nm), which includes visible, infrared, and both UV-A and UV-B spectra (See [Figure 7](#)). The UV-A irradiance meter (Control Co., Friendswood, TX) measured radiation in the 360-390 nm wavelength band ([Figure-7](#)). Both photometers and sensors had been professionally calibrated immediately prior to these experiments. All measurements were made within a closed chamber with a gap only wide enough for wire leads to reach the meters.

The maximum UV-A irradiance observed in the photocatalysis experiments was 1.4 to 1.6 mW·cm⁻², which is considerably less than would be present on a clear day at noon. For

qualitative comparison, the highest measurements recorded outside the laboratory in Vicksburg, MS, during these experiments were between 2.0 and 2.5 $\text{mW}\cdot\text{cm}^{-2}$ at approximately noon.

The experimental broad spectrum was much weaker than would be experienced in natural sunlight. Maximum experimental values were between 3 and 4 $\text{mW}\cdot\text{cm}^{-2}$, whereas noon day sunlight in Vicksburg was often between 1000 and 1200 $\text{mW}\cdot\text{cm}^{-2}$.

Chemical Analyses. All effluent was analyzed for explosives and associated transformation products by a modified US EPA Standard Method 8330 for high-performance liquid chromatography (HPLC). The Agilent 1100 was equipped with a Diode Array detector with wavelength 234 and 254 spectra collected. A ThermoElectron C18 ODS Hypersil reversed phase 100 x 4.6 column was used. Mobile phase flow rate was 1.5 mL/min. The mobile phase was comprised of 68% 20 mMol ammonium chloride in water and 32% methanol:butanol (98:2 v/v).

Microbiology. These demonstration phase experiments focus exclusively on the critical abiotic reaction processes. No special precautions were taken to combat potential microbial growth in the columns and no growth was evident. Acid-washed quartz sand in the columns and the sterile deionized water (18 Ω) are unlikely to introduce or stimulate such activity. However, as self-remediation technologies continue to develop, soil microbial processes will become a critical component in any environmental assessment.



Figure 6. Self-remediation column setup. All columns were Whatman syringless filters (polypropylene; I.D. = 20 mm), packed with quartz sand. Unforced, gravitational drainage passed a 0.45 μm , glass microfiber (GMF) filter, exiting through a luer slip inserted into a hole drilled in the cap of an amber glass collection vial. TiO_2 -amended samples were placed on the sand surface to permit light exposure. Samples with all other amendments were buried at $\sim 2/3$ of column height (~ 8 mL level). Three columns were prepared for each amendment, accompanied by unamended replicates.



Figure 7. Photometers and sensors used in the photodegradation experiments.

The PMA2100 photometer and PMA2141 Pyranometer (left; Solar Light Co., Glenside, PA) measure a broad spectrum (305-2800 nm).

The UV-A irradiance meter (right; Control Co., Friendswood, TX) measures radiation in the 360-390 nm wavelength band.

RESULTS and DISCUSSION

PBXN-107 formulations amended with 5, 10, and 15 weight-percent (wt%) of Fe, Fe:Ni (8:2 m/m), or TiO₂ were subjected to sensitivity testing and self-remediation evaluation. Indications of increased sensitivity were found for each amendment, while no evidence of RDX transformation was detected. The compromised condition of the samples precludes meaningful comparison of amended versus unamended samples, but discouraging results are still informative. These particular amendments to PBXN-107 were not effective. Results of the sensitivity testing, CHEETAH model analyses, and self-remediation experiments are detailed below.

Composition-B amended with 5 volume-percent (v%) of Fe, TiO₂, or Na-dithionite were subjected to self-remediation analysis as a supplemental investigation. No sensitivity analyses were conducted. TNT transformation products were detected in all formulations, while no RDX transformation products were detected by HPLC. The effects of these amendments to Comp-B appear to be insufficient to support effective self-remediation.

Sensitivity Test Results

Impact tests conducted on the PBXN-107 samples indicate a substantial reduction in drop height in the amended specimens relative to the unamended samples (Table 4; Figure 8). The impact height of unamended PBXN-107 was 47.3 cm. The addition of *any* powdered Fe or FeNi reduced the impact height by at least half, to between 20.7 and 23.3 cm. For TiO₂, the impact heights appear to be inversely proportional to the amount amended. The anvil velocity was 8 ft/sec for all trials.

The substantial decrease in the impact test drop height is potentially problematic. However, comparison of these results with the unamended samples is compromised somewhat by the improperly cured nature of the amended preparations. The friable nature of the amended samples may have made these samples more sensitive than they might have been in a properly bound material.

BAM and ABL friction tests revealed no clear trends by amendment type or amount (Table 4). The unamended preparations were considered too coarse for the BAM test, so the ABL friction test was performed. The ABL friction tests showed no reaction in 20 trials at the maximum pressure of the test equipment, *i.e.*, a pin pressure 1800 psi. BAM friction tests were conducted on all of the amended samples (Table 4). No obvious, consistent trends are evident beyond a subjective trend of increased reactivity with increasing amendment level.

Electrostatic sensitivity tests (Table 4) on all 10 samples showed no reactions in 20 trials. Each test applies a charge of 0.25 joule, the maximum energy level of the test apparatus. Clearly, none of the amendments tested appear to increase electrostatic sensitivity of PBXN-107.

The CHEETAH model was used to estimate detonation velocities, among other properties, for only the unamended PBXN-107 and the 5% and 10% amended preparations. As would be expected intuitively, the predicted detonation velocities decrease in proportion to the level of amendment (Figure 9). The metallic amendments are predicted to have a greater effect than TiO₂. This relative effect prediction seems counterintuitive since the dense metallic amendments would displace less RDX than would 5 wt% TiO₂, which would also be inert. The model may not be taking amendment reactivity or density into consideration.

Table 4. Summary of PBXN-107 sensitivity test results					
Amendment	Impact Test ¹ Drop Height (cm)	BAM ² (N)		ABL Friction Test ³	Electrostatic Sensitivity Test, EST ⁴
		React	No Reaction		
Unamended	47.3	Material too coarse		No Reaction ⁵ at 1800 psi (max.)	No Reactions ⁵
Fe – 5%	20.7	240	216		
– 10%	21.1	240	216		
– 15%	21.5	168	160		
FeNi – 5%	20.8	192	168		
–10%	23.2	252	240		
–15%	216	216	192		
TiO ₂ – 5%	36.1	240	216		
–10%	28.7	216	192		
–15%	25.0	216	192		
¹ Impact Test: ELR Type 12 impact tester; 2.5 kg drop-weight. Drop height indicates 50% probability of initiation as indicator of sensitivity.					
² BAM tests friction sensitivity; ~30 mg sample on reciprocating porcelain plate is pressed by porcelain pin (360 N maximum load); pin load is reduced until 10 trials yield no reactions					
³ ABL Friction (unamended only): sample is compressed beneath sliding anvil, which is struck laterally with a known force; pressure increased from 10 psi to 1800 psi until a reaction is detected in 20 trials.					
⁴ EST: 20 trials applying 0.25 J charge, the maximum energy level of test apparatus					
⁵ A reaction would be indicated by visible sparks, flames, audible explosion, loud crackling noise, or detection of reaction products by gas analyzer.					

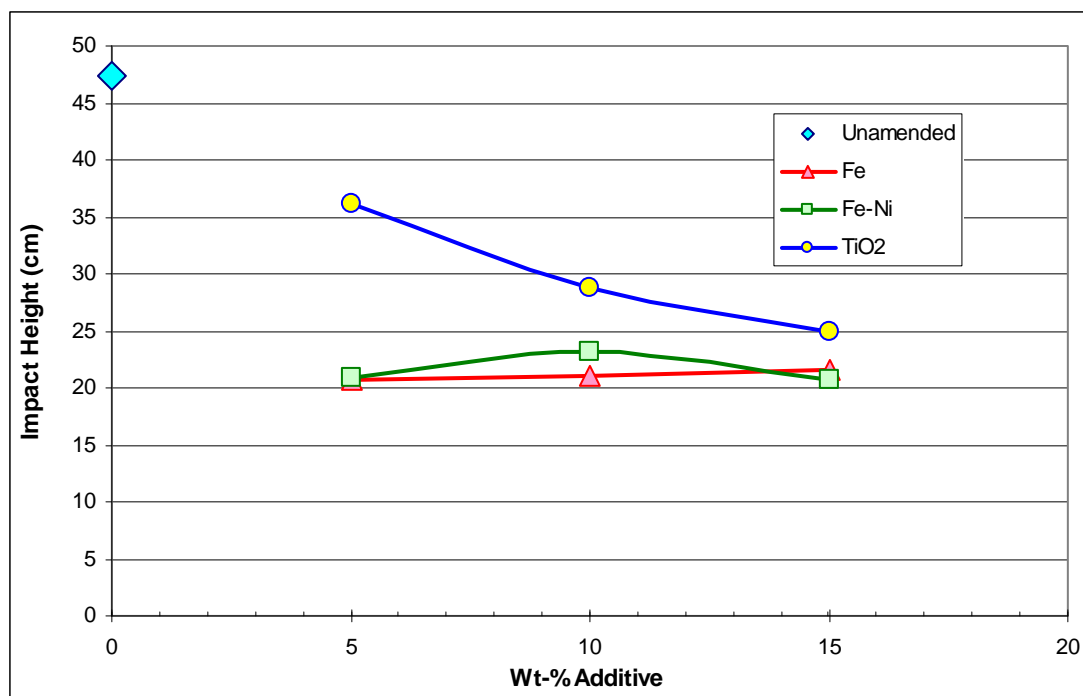


Figure 8. Plot of impact heights for PBXN-107 amended with 5, 10, and 15 weight-% Fe (red triangles), FeNi (green squares), and TiO₂ (yellow circles), relative to unamended material (blue diamond).

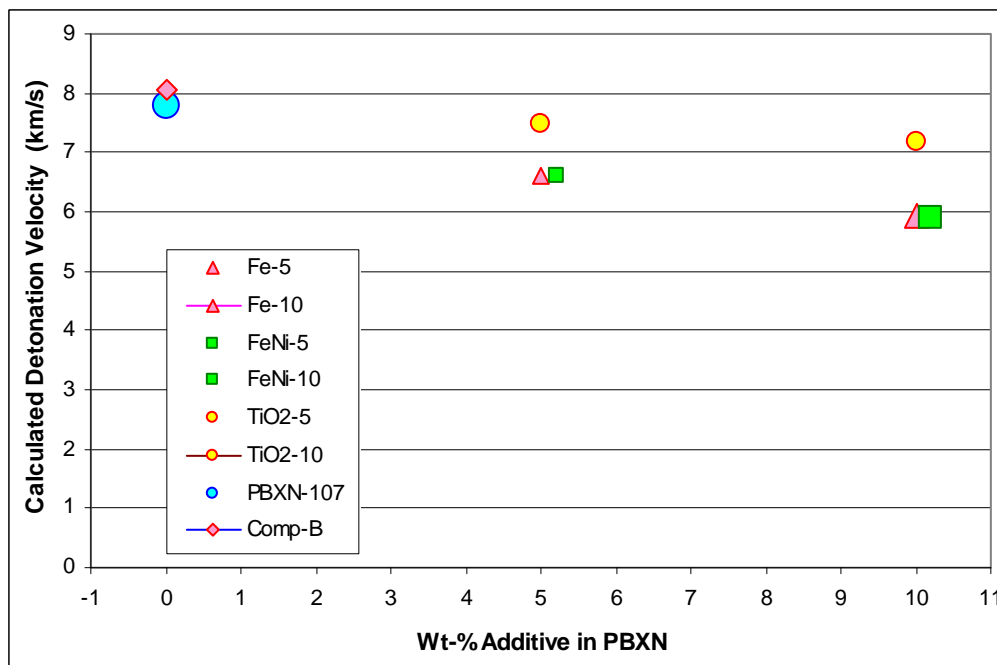


Figure 9. CHEETAH model predictions of detonation velocities for PBXN formulations amended with 5 and 10 weight-% of Fe, FeNi, and TiO₂, compared to unamended PBXN-107 (blue circle) and Composition B (red diamond).

PBXN Self-Remediation Test Results

None of the amendments (Fe, FeNi, and TiO₂) evaluated in PBXN-107 formulations affected the anticipated decreases in RDX concentration in the column effluent. However, the highly variable condition of the amended samples introduced a major source of variability and precludes quantitatively meaningful analysis of the results. These demonstration experiments with PBXN-107 were conducted to evaluate potential enhancement of chemical alteration in the presence of additives, despite the compromised condition of the samples. No such evidence of RDX transformation was detected by HPLC. Results for amended Comp-B were only slightly more encouraging.

Unamended PBXN-107. Experiments with each of the three self-remediation suites included two or three columns with unamended PBXN-107 tablets, or blanks, as a basis for comparison. In all cases, the effluent from these control columns yielded lower or similar concentrations of RDX and no indication of transformation products.

The two unamended blanks associated with the Fe-amended experiments yielded approximately 18 ppm RDX during the first two weeks (Figure 10). After an extended drying out period to assess weight loss, these columns were re-wetted. The effluent concentrations increased slightly at first, but quickly decreased and leveled off at concentrations just under 10 ppm. Similarly, the initial effluent (first 6 days) from the two unamended PBXN-107 tablets in the FeNi-amended suite had average RDX concentrations of 10-15 ppm, which decreased to 5-10 ppm for the remainder of the 34-day experiment (Figure 11).

Three columns with unamended PBXN-107 were included in the TiO₂-amended suite. The RDX effluent from these columns was less than observed for the metallic suites, with an early average of 10 ppm, drifting steadily downward to 4-5 ppm by day-38 (Figure 12). These lower RDX concentrations are to be expected for the photocatalyst experiments because the samples sat on the column surface and therefore not surrounded by pore-water which could affect continuous dissolution between wetting or flushing events. At least the tops of the TiO₂ suite samples were able to dry out between wetting events.

Mass decreases in the unamended sample columns over the course of the experiments are attributed to RDX dissolution. Mass loss (± 1 std. dev.) in the unamended samples in the Fe-suite averaged $4.49 \pm 0.09\%$ (30 days; with interruption). Curiously, similar experiments with FeNi-suite averaged $10.45 \pm 0.01\%$, though these did run continuously for 33 days. The unamended samples in the TiO₂-amended suite showed a mass loss of $12.63 \pm 0.71\%$ over 38 days. Comparisons of these 3 sets of unamended preparations are complicated by differences in experiment duration, temperature, or wetting conditions.

PBXN-107 Amended with Powdered Fe. Effluent from the Fe-amended PBXN-107 showed a very similar trend as the unamended samples, but at higher concentrations (Figure 10). All three levels of amendment showed average effluent concentrations between 23 and 27 ppm during the initial wetting phase. Only the 10 and 15% Fe columns were continued after the dry-out period and these showed a similar trend as the unamended samples (Figure 10). Higher RDX concentrations in the effluent from the amended material columns may seem counterintuitive, but this is most likely to be an artifact of the less consolidated condition of the amended materials (Figure 2). No RDX transformation products were detected in effluent from any of the Fe-amended suite columns.

PBXN-107 Amended with Powdered FeNi. Average RDX concentrations in the effluent from the FeNi-amended columns started out between 19 and 25 ppm, and decreased to level off between 13 and 17 ppm (Figure 11). These RDX concentrations are a bit higher than observed for the Fe-amended materials. FeNi-amended samples were the most friable of the amendments considered (see Figure 2). These observations are consistent with the intuitive suggestion that increased sample friability would expose more RDX crystallite surfaces to be dissolved into the aqueous phase.

Clearly, there was no obvious reduction in RDX effluent concentration with FeNi amendments. None of the simple reduction reaction intermediates of RDX (MNX, DNX, and TNX) were detected in the effluent by HPLC. The hypothesized enhancement of RDX reduction by the addition of Ni to the powdered metal additive is not supported. However, it would be premature to reject the hypothesis, given the compromised nature of the samples.

Isothermal Conditions for Fe and FeNi PBXN Experiments. Temperatures remained effectively uniform in the dark enclosure during the separate evaluations of the Fe-amended PBXN (Figure 12A) and the FeNi-amended PBXN (Figure 12B). All temperature measurements were between 16 and 22 °C. Average temperature (± 1 std. dev.) for the Fe-PBXN test was 18.7 ± 1.6 °C, though the initial temperatures appear to be a few degrees warmer than later in the experiment, reflecting ambient changes during the dry-out period. Temperatures during the continuous experiment with FeNi amendments were very consistent, with an average temperature (± 1 std. dev.) of 17.4 ± 0.5 °C.

Mass Loss in Fe and FeNi PBXN Experiments. RDX mass loss due to dissolution over the course of the experiments shows some consistent, general trends. Initial mass, mass loss, and percent mass loss in columns of the Fe-amended suite are summarized in Table 5. Samples began in various stages of disaggregation and could not reliably be recovered fully from the columns in order to assess mass loss directly. Columns were weighed at each stage of construction to quantify initial sample mass. Upon conclusion of the experiments, the columns were dried for an extended period on an open hot plate (80 °C) until masses approached a stable value, with care taken not to melt the columns.

Within-treatment replication appears to be good. Differences between treatments are small but mirror the observations of effluent concentrations. The unamended samples showed the lowest percent mass loss, consistent with their having the lowest concentration of RDX in the effluent. The 15%-Fe samples narrowly showed the greatest average mass loss, also with the greatest variability in mass loss, yet the effluent concentrations were intermediate. The trend is more noticeable in the FeNi-amended suites (see Table 6), with the 15% level showing both the greatest mass loss and greatest effluent concentrations.

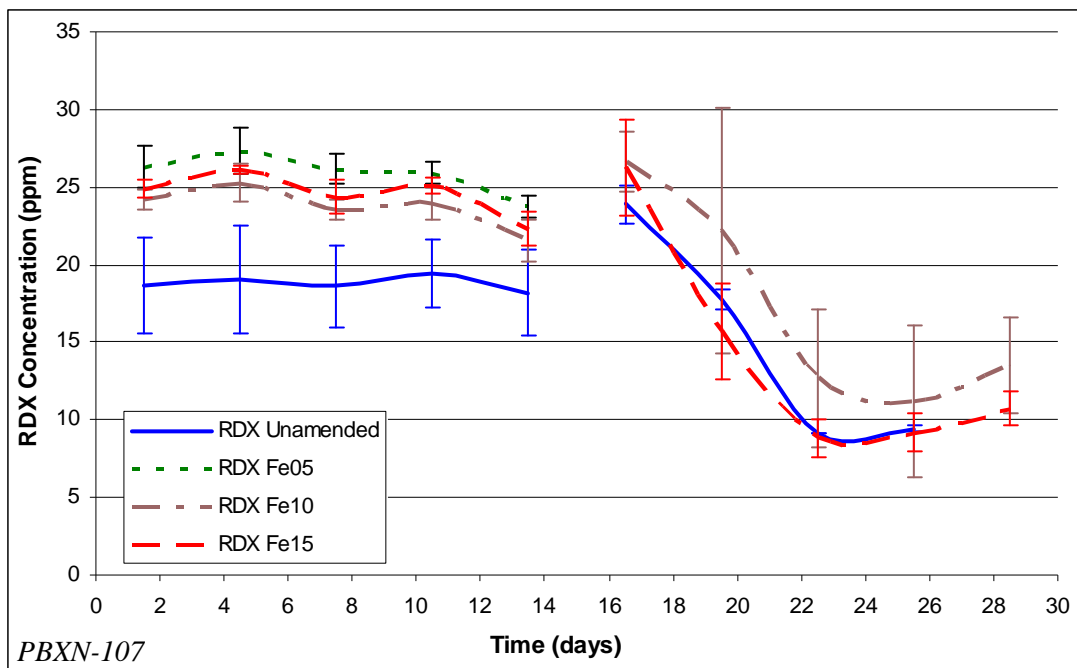


Figure 10. Trends in RDX effluent from PBXN-107 amended with 5, 10, and 15 weight-percent powdered iron. Vertical bars indicate ± 1 standard deviation ($n=3$). The break in trend-lines represents an extended dry-out period to assess mass loss before resumption of self-remediation testing. Amended samples displayed varying levels of non-consolidation.

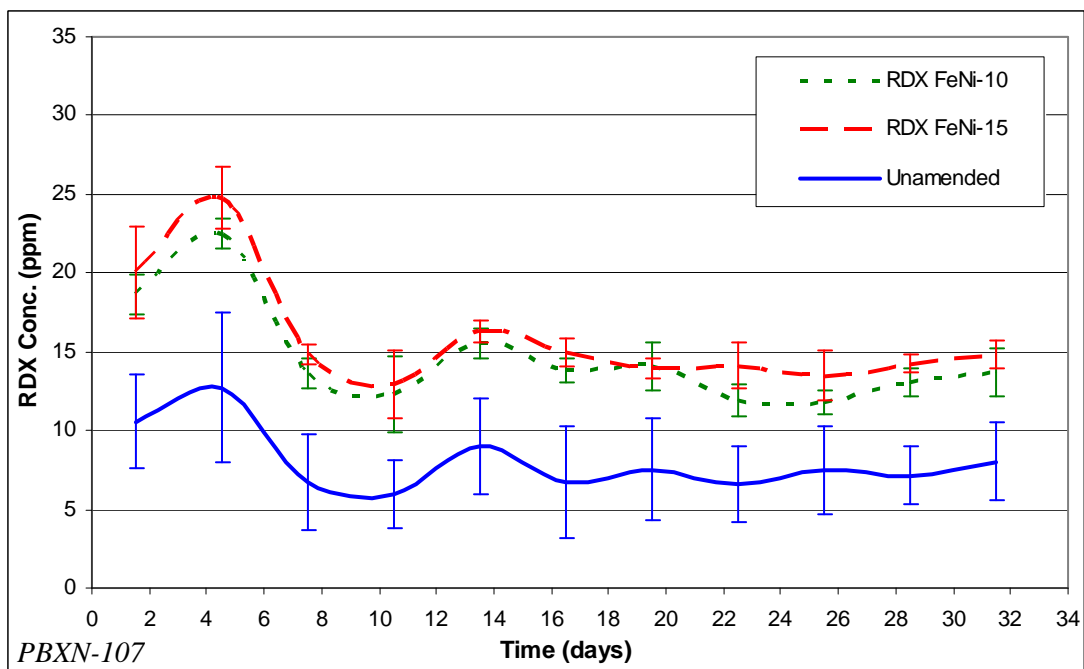


Figure 11. Trends in RDX effluent from PBXN-107 amended with 10 and 15 weight-percent powdered iron-nickel (80Fe:20Ni). Vertical bars indicate ± 1 standard deviation ($n=3$). All FeNi-amended samples were highly friable.

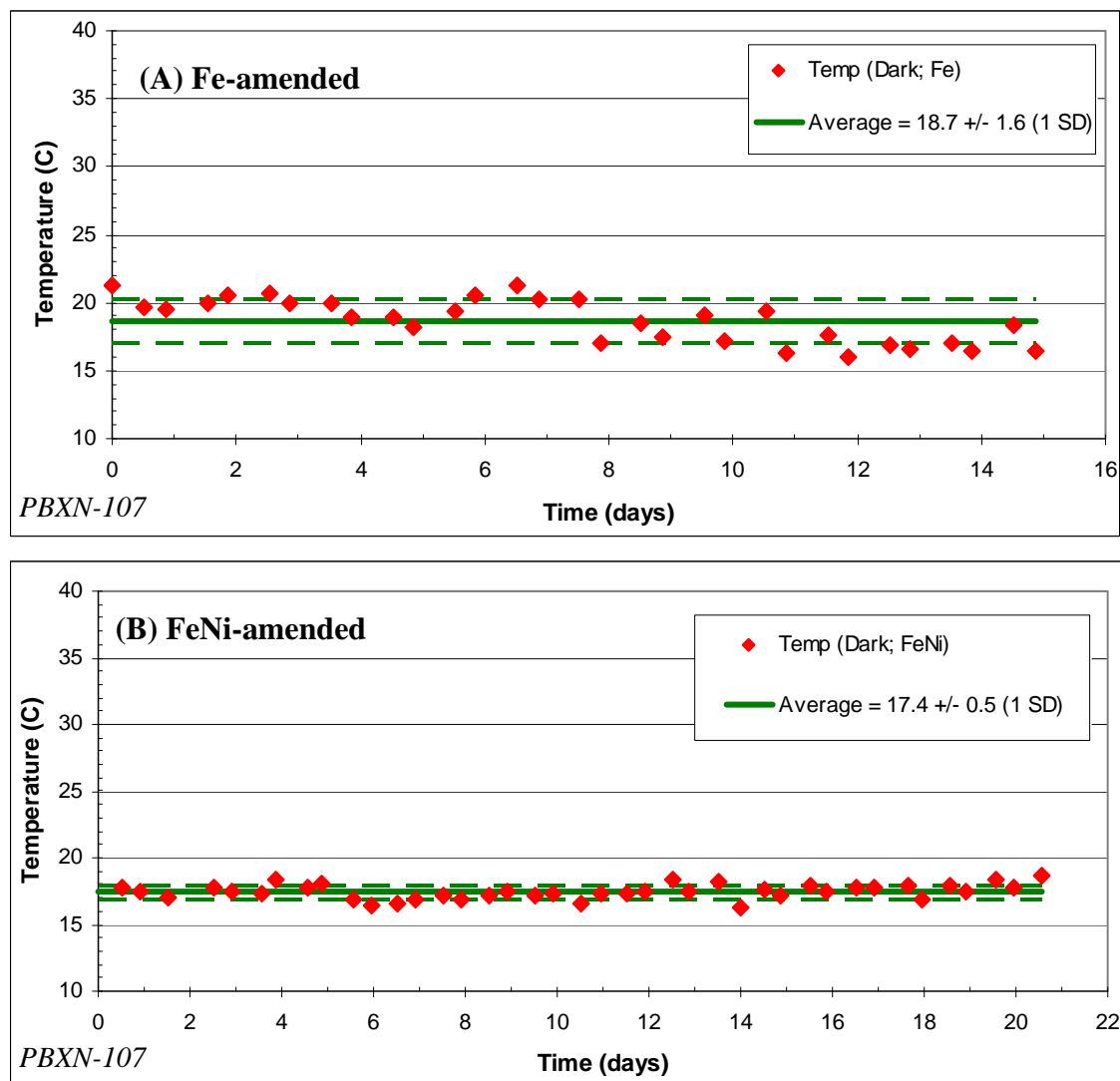


Figure 12. Temperature trends within the dark chamber during evaluation of PBXN-107 amended with (A) iron, and (B) iron-nickel. No temperature control was imposed other than isolation.

Table 5. Summary of mass changes in PBXN-107 amended with powdered Fe (30 days)

Sample		Initial Mass ¹ (g)	Mass Loss ² (g)	Percent Mass Loss
Unamended	B1	0.6260	0.0285	4.55%
	B2	0.6574	0.0291	4.43%
		Avg. \pm Std. Dev.:	0.0288 \pm 0.0004	4.49 \pm 0.09%
Fe-Amended	5A ³	0.5716	0.0204	3.57%
	5B ³	0.5857	0.0186	3.18%
	5C ³	0.5793	0.0184	3.18%
		Avg. \pm Std. Dev.:	0.0191 \pm 0.0011	3.31 \pm 0.23%
	10A ⁴	0.6450	Terminated	
	10B	0.6166	0.0294	4.65%
	10C	0.5892	0.0302	4.74%
		Avg. \pm Std. Dev.:	0.0283 \pm 0.0006	4.69 \pm 0.06%
	15A	0.7605	0.0332	4.50%
	15B	0.5941	0.0342	5.62%
	15C	0.6924	0.0334	4.85%
		Avg. \pm Std. Dev.:	0.0336 \pm 0.0005	4.99 \pm 0.56%

¹Mass determined by difference as components added to column.

²Mass loss of entire column after extended drying is attributed to explosives dissolution.

³The 5% series was terminated after the initial wetting period (15 days)

⁴Column 10A was terminated due to sand mass loss

Table 6. Summary of mass changes in PBXN-107 amended with FeNi (33 days)

Sample		Initial Mass ¹ (g)	Mass Loss ² (g)	Percent Mass Loss
Unamended	B3	0.7152	0.0747	10.44%
	B4	0.6581	0.0688	10.45%
		Avg. \pm Std. Dev.:	0.0717 \pm 0.0042	10.45 \pm 0.01%
FeNi-Amended	10A	0.6181	0.0638	10.32%
	10B	0.6378	0.0669	10.49%
	10C	0.6468	0.0684	10.58%
		Avg. \pm Std. Dev.:	0.0664 \pm 0.0023	10.46 \pm 0.13%
	15A	0.6959	0.0677	9.7284
	15B	0.5546	0.0630	11.36%
	15C	0.5081	0.0672	13.23%
		Avg. \pm Std. Dev.:	0.0660 \pm 0.0026	11.44 \pm 1.75%

Only the 10 and 15 wt% FeNi suites were tested.

¹Mass determined by difference as components added to column.

²Mass loss of entire column after extended drying is attributed to explosives dissolution

PBXN-107 Amended with TiO₂. Trends in the effluent RDX concentrations in the TiO₂-amended PBXN suite support, more strongly than do the other two amendments, the contention that sample condition strongly affects dissolution. The most consolidated of the TiO₂-amended PBXN samples are at the 5% level, and the least consolidated (most friable) samples contain 15% TiO₂ (see [Figure 2](#)). RDX concentrations in leachate from the 5% amended samples are virtually indistinguishable from the unamended samples ([Figure 13](#)). In strong contrast, RDX in the effluent from the highly friable 15% samples show strikingly higher concentrations between 17 and 40 ppm, approaching the solubility of RDX. PBXN replicates amended with 10% TiO₂ show intermediate levels of both friability ([Figure 2](#)) and RDX concentrations in the effluent ([Figure 13](#)). No transformation products were indicated in any of the effluent analyzed only by HPLC.

Light radiation was altered twice during the course of experiments with the TiO₂-amended PBXN-107. In both cases, the intent was to increase the intensity of UV radiation at the sample surfaces in order to promote phototransformations if possible. Increasing the UV-A radiation was also intended to more closely approach levels from natural sunlight. At day-9 and day-13 the samples were raised closer to the light sources. This resulted in the expected increases in temperature ([Figure 14A](#)), UV-A radiation ([Figure 14B](#)), and broad spectrum radiation ([Figure 14C](#)). The initial light source included one UV-A bulb and one broad spectrum plant bulb. At day-9, the plant bulb was replaced with a second UV-A bulb. At day-13, one of the UV-A bulbs was replaced with a UV-B bulb. Photodegradation experiments with Comp-B also used this final light source configuration.

The increase in temperature with closer proximity to the light source did not appear to have a substantial impact on the dissolution or degradation of RDX. The concentrations of RDX in the leachate actually decrease gradually with time, despite the overall 10 °C increase in temperature. This counterintuitive trend may reflect increasingly rapid evaporation of applied water, perhaps with recrystallization of RDX, though none was evident macroscopically.

Mass Loss in TiO₂ PBXN Experiments. Differences in percent mass loss are small ([Table 7](#)), but generally consistent with effluent concentration trends. The highly friable 15% TiO₂ samples showed the greatest mass loss as well as dramatically greater effluent concentrations.

Table 7. Summary of mass changes in PBXN-107 amended with TiO ₂ (38 days)				
Sample		Initial Mass ¹ (g)	Mass Loss ² (g)	Percent Mass Loss
Unamended	TBA	0.7490	0.0918	12.26%
	TBB	0.7497	0.0914	12.19%
	TBC	0.7134	0.0960	13.46%
		Avg. ± Std. Dev.:	0.0931 ± 0.0025	12.63 ± 0.71%
TiO ₂ -Amended	5A	0.8740	0.1013	11.59%
	5B	0.8318	Terminated early (column mass loss)	
	5C	0.9361	0.0984	10.51%
		Avg. ± Std. Dev.:	0.0999 ± 0.0021	11.05 ± 0.76%
	10A	0.7033	0.1022	14.53%
	10B	0.9087	0.1130	12.44%
	10C	0.6999	0.1016	14.52%
		Avg. ± Std. Dev.:	0.1056 ± 0.0064	13.83 ± 1.21%
	15A	0.6383	0.0950	14.88%
	15B	0.6853	0.0999	14.58%
	15C	0.7045	0.0963	13.67%
		Avg. ± Std. Dev.:	0.0971 ± 0.0025	14.38 ± 0.63%

¹Mass determined by difference as components added to column.
²Mass loss of entire column after extended drying is attributed to explosives dissolution

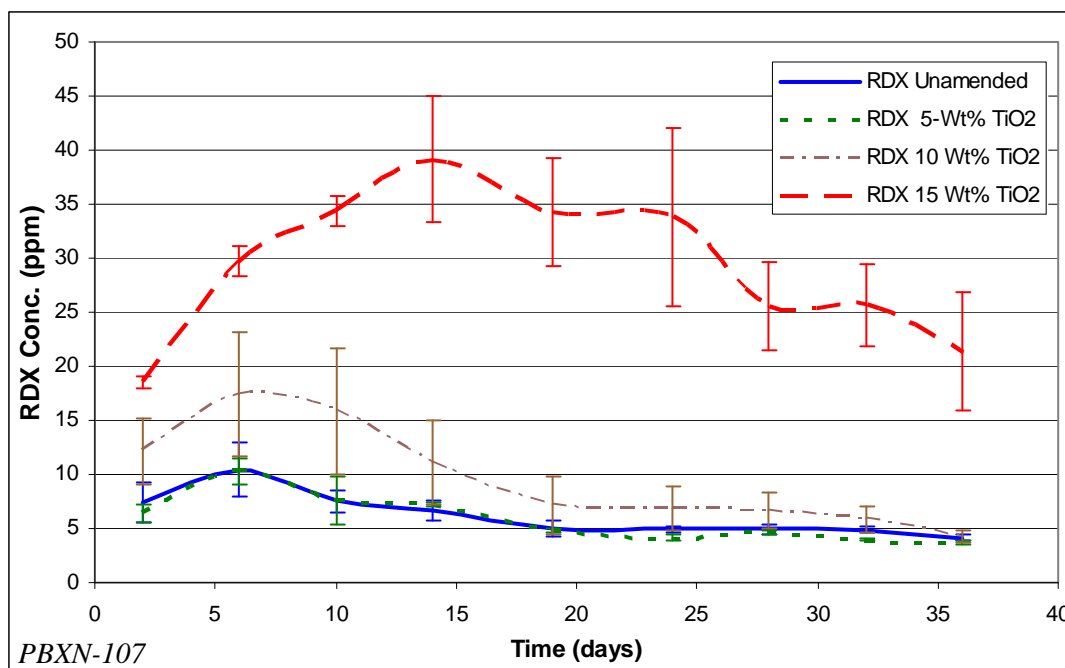


Figure 13. Trends in RDX effluent from PBXN-107 amended with 5, 10, and 15 weight-percent anatase TiO₂ (doped with 3 wt% WO₃). Vertical bars indicate ±1 standard deviation (n=3). Sample friability increased with increasing TiO₂ amendment

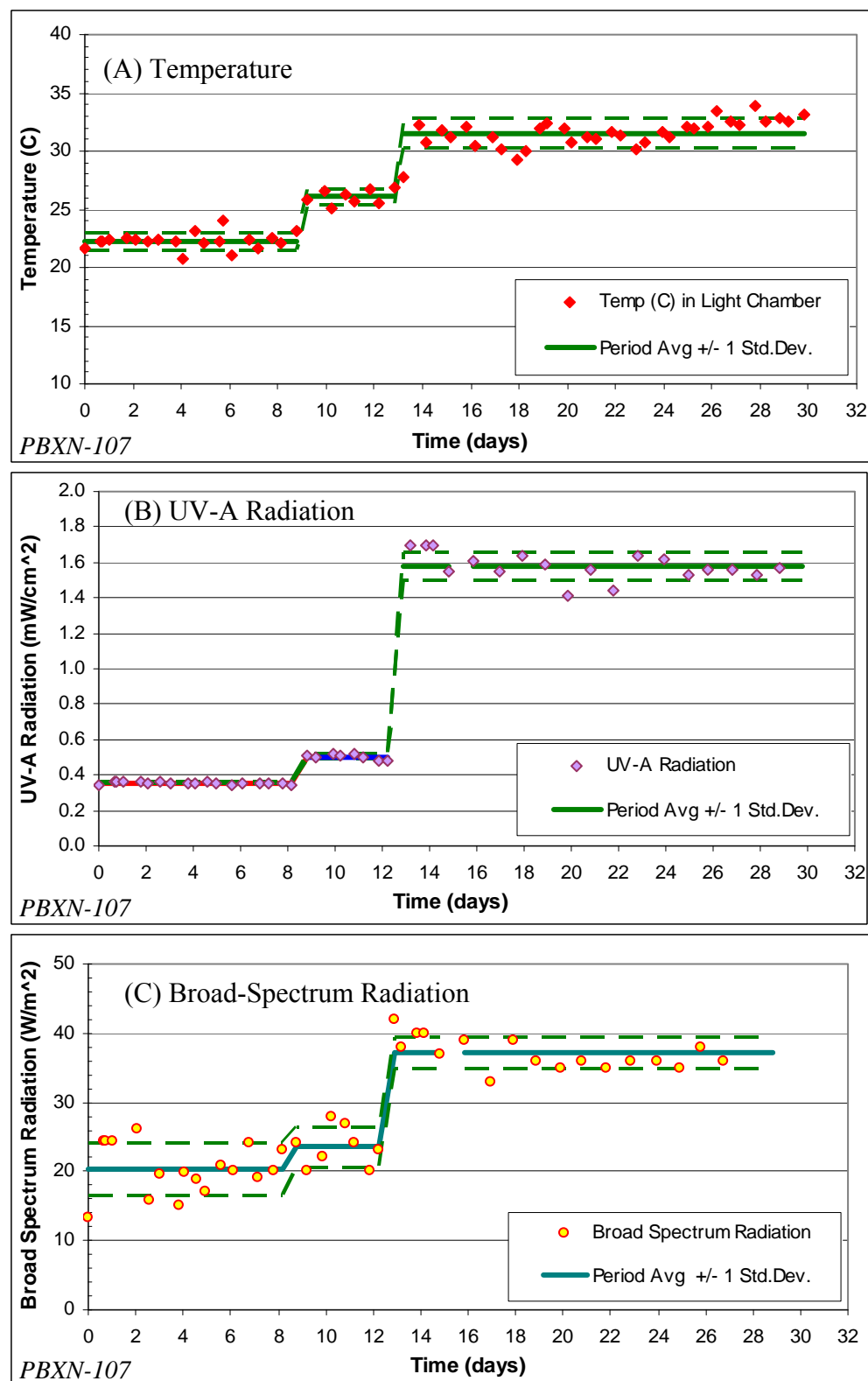


Figure 14. Temporal trends in (A) temperature, (B) UV-A irradiance, and (C) Broad-spectrum radiation for the lighted experiments with TiO₂-amended PBXN-107. Symbols indicate measurements; solid lines indicate averages for each of the 3 lighting conditions; dashed lines delineate ± 1 std. dev. for each period. The step increases reflect a progressive elevation of samples toward the light source (distances of 38.8, 23.5, and 7.5 cm) and full UV-A light sources (see text). Note that $10 \text{ W/m}^2 = 1.0 \text{ mW/cm}^2$.

Composition B Self-Remediation Results

Self-remediation analyses of the amended Composition-B were slightly more encouraging than the PBXN results in that: (1) amendments did not interfere with sample cohesiveness or physical stability, (2) sample preparations were much more uniform with respect to explosives mass and exposed surface area, and, most importantly (3) TNT transformation products were detected. Although the dithionite amendment had the greatest impact in terms of transformation product generation, none of the three amendments considered were able to noticeably impact the concentration of TNT or RDX in the effluent.

Samples from the dark experiments remained intact throughout the experiments (Figure 15) and could be recovered from all columns for direct determination of mass loss. However, the samples that were exposed to light generated an unidentified surficial material that was prone to spalling off (see Figure 20).

Low and fairly constant levels of HMX were detected in the effluent of both amended and unamended Comp-B. HMX is to be expected as a minor component in any formulation that includes RDX. Replicate averaged HMX concentrations remained between 1 and 2 ppm in the dark experiments (unamended and Fe- or dithionite-amended), but were consistently lower (0.4 to 0.9 ppm) in the lighted experiments (unamended or TiO₂-amended). The greater HMX concentrations in effluent from the dark columns are likely due to the more persistent wetting of the buried samples compare to the samples placed on top of the column in the lighted experiments. None of the amendments appear to have facilitated transformation of HMX.

Low and gradually decreasing concentrations of 2,4-DNT were also detected in effluent from both unamended and amended Comp-B. As with HMX, effluent from the dark experiments generated greater concentrations of 2,4-DNT than the photodegradation experiments. Replicate-averaged, 2,4-DNT concentrations from the unamended and Fe-amended dark columns ranged from 0.43 ppm to below detection. Effluent from the dithionite-amended material followed a similar trend, but ranged from 1.58 to 0.31 ppm. The slightly greater concentrations of 2,4-DNT, as well as HMX, in the effluent from the dithionite-amended material may reflect an increase in exposed surface area of explosives as the more soluble dithionite was leached out early, generating tiny pock marks in the surface. In contrast, only two replicate-averaged effluent values from early in the lighted experiments were above detection, and these were 0.1 ppm or less. Neither 2,4-DNT nor HMX are plotted in the figures below as they do not contribute substantially to the assessment of Comp-B self-remediation.

All column experiments were conducted in triplicate. HPLC analyses may not detect a particular constituent in one or more of the replicates, particularly if concentrations are very low. If a constituent is detected in only one of the three replicates, it is not amenable to statistical analysis and is presumed absent. Of the 132 total data points plotted below for the Comp-B analyses, only four TNB and two 4A-DNT points were neglected in this fashion. If the constituent is detected in two or more replicates, then the results are included in the effluent trend plots below.

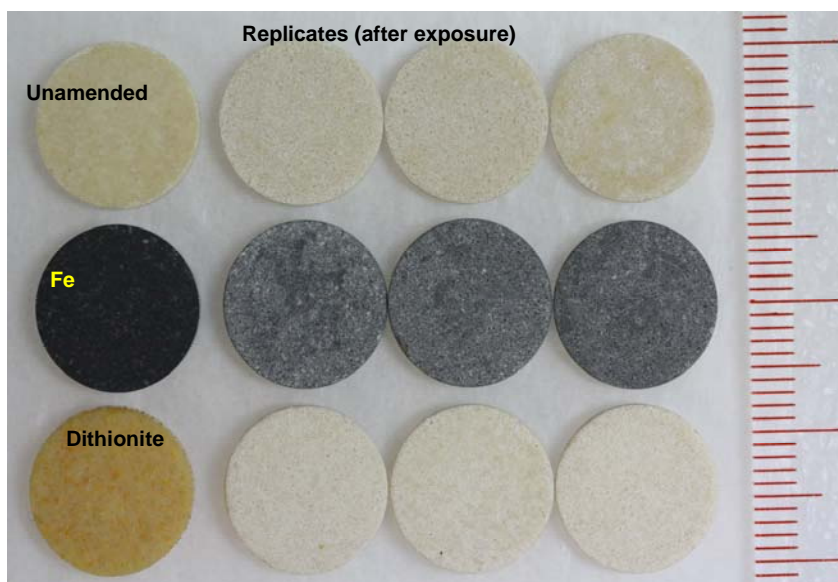


Figure 15. Composition-B tablets prior to exposure (leftmost disks) and the three replicates after exposure to intermittent flushing in packed columns. Unamended samples are in the top row, Fe-amended samples are in the middle row, and dithionite-amended samples are in the bottom row.

Dark Experiment Results

Unamended Comp-B in Dark Experiments. Replicate-averaged TNT concentrations in the effluent from the unamended Comp-B columns ranged between 30 and 41 ppm, but showed no clear trend over time (Figure 16). RDX showed similar behavior at lower concentrations, between 12.3 and 16.2 ppm. No 4A-DNT and only traces of TNB were detected in the effluent.

Fe-amended Comp-B. Temporal trends in the effluent from the columns with Fe-amended Comp-B (Figure 17) were quite similar to the unamended trends. TNT averages ranged between 35.9 and 42.9 ppm; RDX ranged between 13.8 and 16.3 ppm. Only very low levels of TNB were detected, quite similar to the unamended effluent, suggesting that TNB may be a trace component in the parent material. No 4A-DNT was detected in the effluent until the last sample; this was surprising considering the effectiveness of carbonyl Fe powder in degrading dissolved explosives. It may be that the explosives are present in such tremendous excess that the iron particles are simply overwhelmed and effectively passivated as reactive surfaces.

Dithionite-amended Comp-B. The Na-dithionite amendment generated more 4A-DNT than any of the other treatments and did so throughout the experiment (Figure 18). The initial replicate-averaged concentration was 5.6 ppm, but effluent concentrations quickly settled between 3.3 and 2.7, with concentrations decreasing gradually with time. A trace amount of TNB was detected in the first sample, similar to other treatments, but not in subsequent samples. Effluent TNT ranged between 39.2 and 53.1 ppm; RDX ranged between 20.6 and 24.6 ppm. The elevated TNT and slightly elevated RDX concentrations, relative to the unamended samples, may reflect a small increase in exposed surface area of explosives as the more soluble dithionite was dissolved to create a more pocked surface.

These dark experiments with Composition B were run simultaneously. Chamber temperature remained effectively constant at 21.2 ± 0.5 °C (Figure 19).

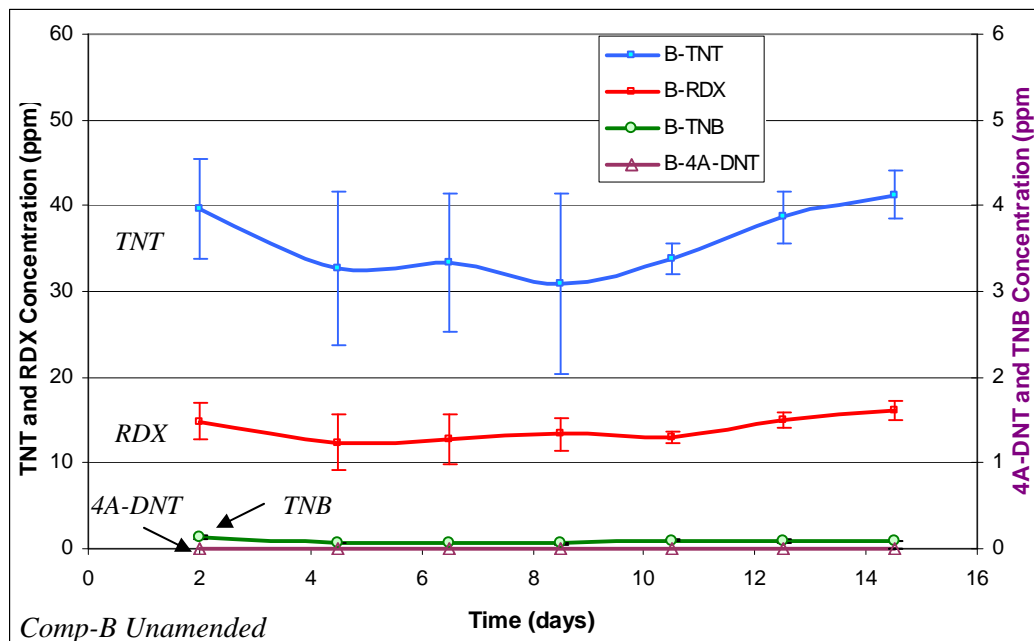


Figure 16. Effluent trends from unamended Comp-B for comparison against Fe- and dithionite-amended equivalents. Note that 4A-DNT and TNB use the expanded scale on the right.

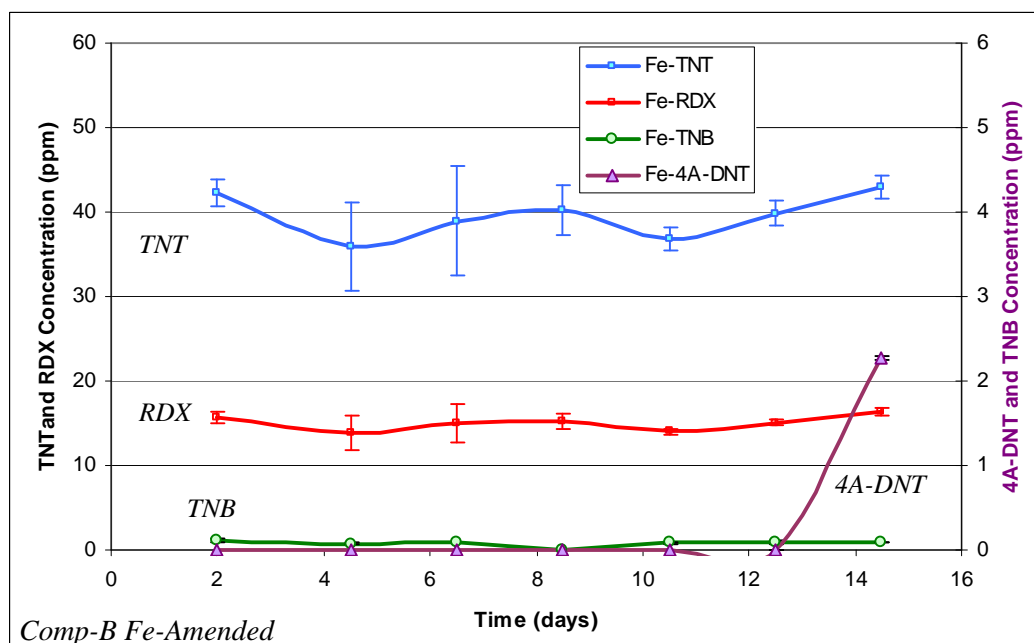


Figure 17. Effluent trends from Comp-B amended with Fe. Note that 4A-DNT and TNB use the expanded scale on the right.

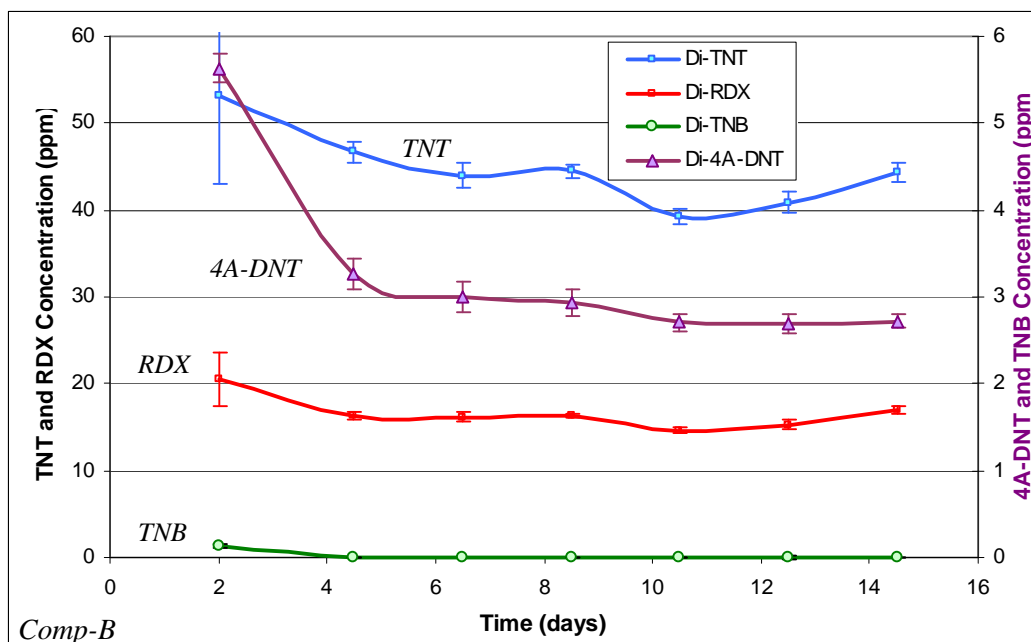


Figure 18. Effluent trends from Comp-B amended with Na-Dithionite. Note that 4A-DNT and TNB use the expanded scale on the right.

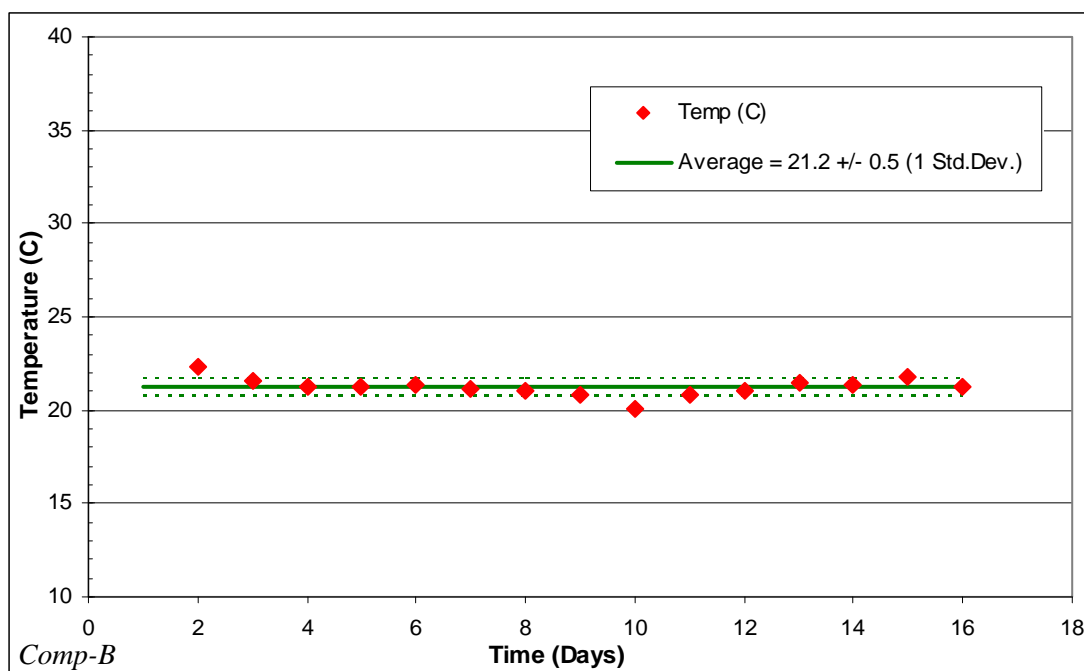


Figure 19. Temperature trends in dark chamber during the assessment of Fe- and dithionite-amended Comp-B, as measured in a water reservoir.

Mass Loss in Comp-B Dark Experiments. Mass loss within replicate groups was remarkably uniform, with standard deviations less than 0.10% (Table 8). Uniform preparation and high sample integrity certainly contributed to this consistency. Percent mass loss was very similar for the unamended and Fe-amended suites (~1%), consistent with the suggestion that the loss is attributable to explosives dissolution. The slightly greater mass loss from the Fe-amended samples may be attributable to minor differences in explosives crystallite sizes or fracturing due to the presence of rigid amendments.

The mass loss in the dithionite-amended suite was much greater than the other dark suites. This contrast is due only in part to the greater aqueous solubility of Na-dithionite relative to other components. The average mass loss of 0.0428 g (8.16%) is greater than the initial dithionite present (0.0338 g; 6.3 wt%; see Table 3) and it is unlikely that more than a small fraction of the dithionite near the sample surface was dissolved during the experiment. Even if all dithionite was leached, the remaining average mass loss would still be 0.0090 g, which is twice that observed for the other suites. A more detailed and thorough analysis of these intriguing differences must be deferred for an investigation of broader scope, *e.g.*, monitoring total sulfur in the effluent.

Table 8. Summary of mass changes in Composition B amended with 5 volume-% of Fe or dithionite				
Sample		Initial Mass ¹ (g)	Mass Loss ² (g)	Percent Mass Loss
Unamended	BA	0.4917	0.0046	0.94%
	BB	0.4880	0.0049	1.00%
	BC	0.4923	0.0041	0.83%
		Avg. \pm Std. Dev.:	0.0045 \pm 0.0004	0.92 \pm 0.09%
Fe-Amended	Fe-A	0.5900	0.0055	0.93%
	Fe-B	0.5915	0.0055	0.93%
	Fe-C	0.5921	0.0057	0.96%
		Avg. \pm Std. Dev.:	0.0056 \pm 0.0001	0.94 \pm 0.02%
Dithionite-Amended	Di-A	0.5233	0.0425	8.12%
	Di-B	0.5237	0.0433	8.27%
	Di-C	0.5258	0.0426	8.10%
		Avg. \pm Std. Dev.:	0.0428 \pm 0.0004	8.16 \pm 0.09%
¹ Initial tablet mass determined by weight gain to column during construction.				
² Final tablet mass obtained by direct measurement after recovery and drying.				

Comp-B Photodegradation Experiment Results

Both unamended and TiO₂-amended Comp-B showed unequivocal visual evidence of alteration due to the persistent light exposure. All samples developed a brown to very dark brown crust on their exposed surfaces (Figure 20). The chemical nature of the brown material remains uncertain, but it appears to have some very limited mobility as the brown stains do not extend beyond close proximity to the sand surface (Figure 21). This sort of alteration is typical for Comp-B fragments exposed to natural sunlight under field conditions, where they take on the appearance of red clay pot shards. The pronounced discoloration banding in these laboratory samples resembles the weaker Liesegang-like banding seen in some field-exposed samples. The stronger banding in the laboratory samples may be an artifact of the wetting procedure which involve dropwise application to the center of the nearly horizontal disk, which could induce preferential dissolution and weathering at the center to form a slight depression where subsequent droplets could pond and evaporate.

Unamended Comp-B in the Photodegradation Experiments. Replicate-averaged concentrations of TNT in the effluent from unamended Comp-B stayed between 4.0 and 4.7 ppm until the last sample with 2.8 ppm (Figure 22A). Similarly, RDX concentrations gradually decrease from 2.6 to 1.0 ppm.

TNB, one of the signature products of TNT photodegradation, is detected in only a few analyses and at trace levels below that detected in the dark experiments (~0.1 ppm). However, these relatively low concentrations are consistent with the less aggressive dissolution environment of the cyclically-wet light experiments compared to the perpetually-wet dark experiments. Trace amounts of 4A-DNT is detected in 3 of the later analyses, all averages below 0.26 ppm.

TiO₂-amended Comp-B. The replicate-averaged concentrations of TNT in the effluent from TiO₂-amended Comp-B show a similar trend as the unamended suite, with 4 of the first 5 analyses between 4.0 and 4.9 ppm (3.6 ppm in the first sample), decreasing to 2.8 ppm in the last sample (Figure 22B). RDX concentrations also follow trend very similar to the unamended suite, with early samples between 2.4 and 2.6 ppm, gradually decreasing to 1.1 ppm.

TNB is present in the early effluent at concentrations between 0.12 and 0.17 ppm. These concentrations, small as they are, are consistent with increased phototransformation of TNT, particularly if the wetting regime is factored into consideration. TNB in the dark experiments were generally below 0.1 ppm. As a crude approximation, only for purposes of comparison, note that the TNT concentrations in the unamended dark experiments are approximately 7.8 times greater than those in the unamended light experiments (~35ppm/4.5ppm). Applying this ratio to the TNB concentrations in the dark experiments, the lighted experiments should have less than 0.02 ppm TNB. This analysis suggests that TNB is being created in the phototransformation experiments and that TiO₂ enhances the transformation, at least in the early stages of exposure. The subsequent decrease in TNB concentrations suggests that the Comp-B fragment surface becomes shaded and/or the photocatalysts become occluded by the brown residue. Finally, the 4A-DNT concentrations are above detection only in the latter stages, similar to the unamended suite, with a suspect spike to 2.2 ppm in the fourth sample replicates.

The trend in UV-A irradiance (Figure 23B) shows a small decrease from an average (± 1 std. dev.) of 1.351 ± 0.025 to 0.990 ± 0.019 mW·cm² at day-16, when one of the two UV-A bulbs was replaced with a UV-B bulb in order to assess impact of higher energy UV radiation. The

bulb change affected a very minor increase in temperature from 34.49 ± 0.66 to 34.56 ± 0.78 °C (Figure 23A), and a small but noticeable increase in broad spectrum irradiance from 3.382 ± 0.132 to 3.625 ± 0.116 mW·cm² (Figure 23C). The higher temperatures in the lighted experiments would be expected to enhance dissolution slightly, relative to the dark experiments, which is another factor that complicates direct comparisons.

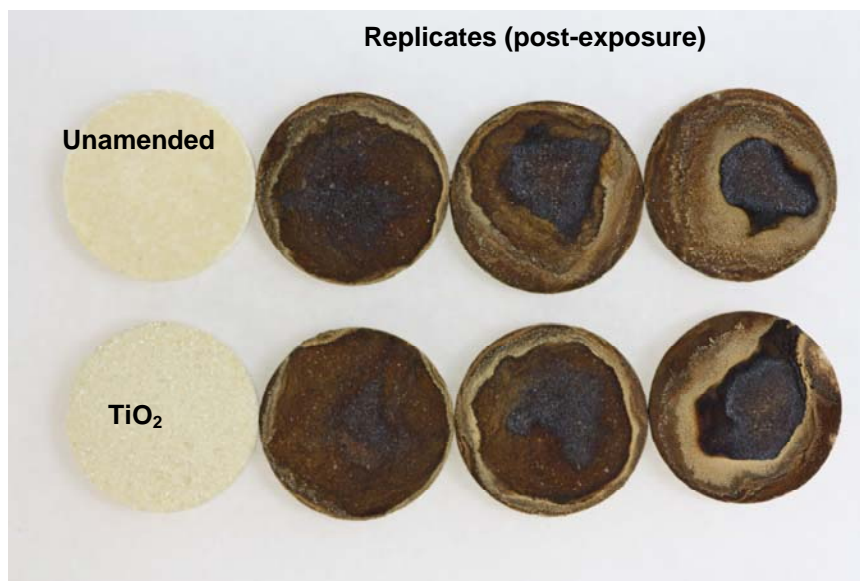


Figure 20. Composition B disks prior to exposure (light-colored disks to left) and after exposure to light. Initial disk diameters were 13 mm.



Figure 21. Profiles of several columns that had contained Comp-B disks developed a brown residue at the surface after light exposure.

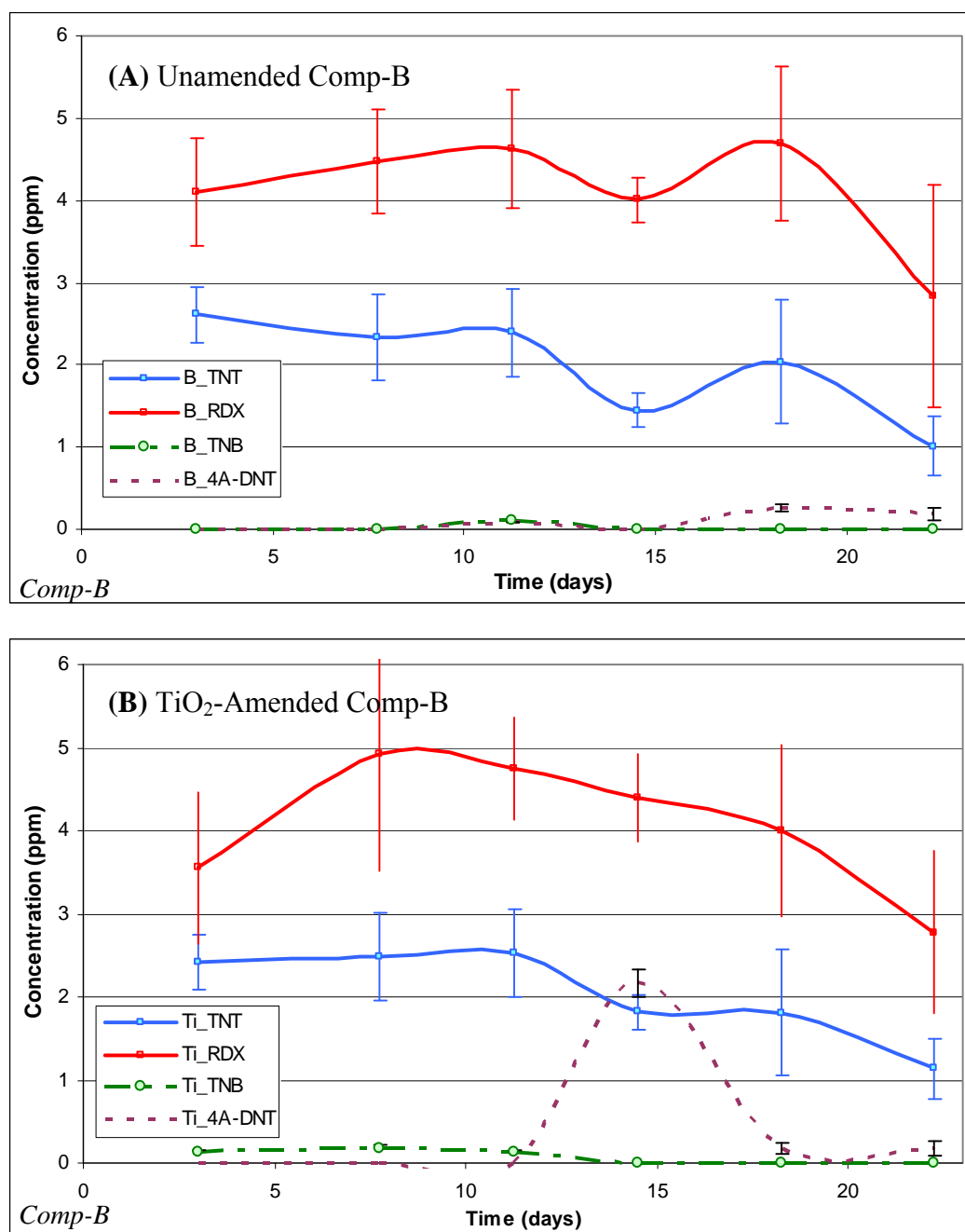


Figure 22. Effluent trends from unamended (A; top) and TiO₂-amended (B; bottom) Comp-B under persistent light conditions (see Figure 23). All constituents use right scale, which has the same range as the right scale in the previous figures for the dark experiments (Fe and dithionite amendments).

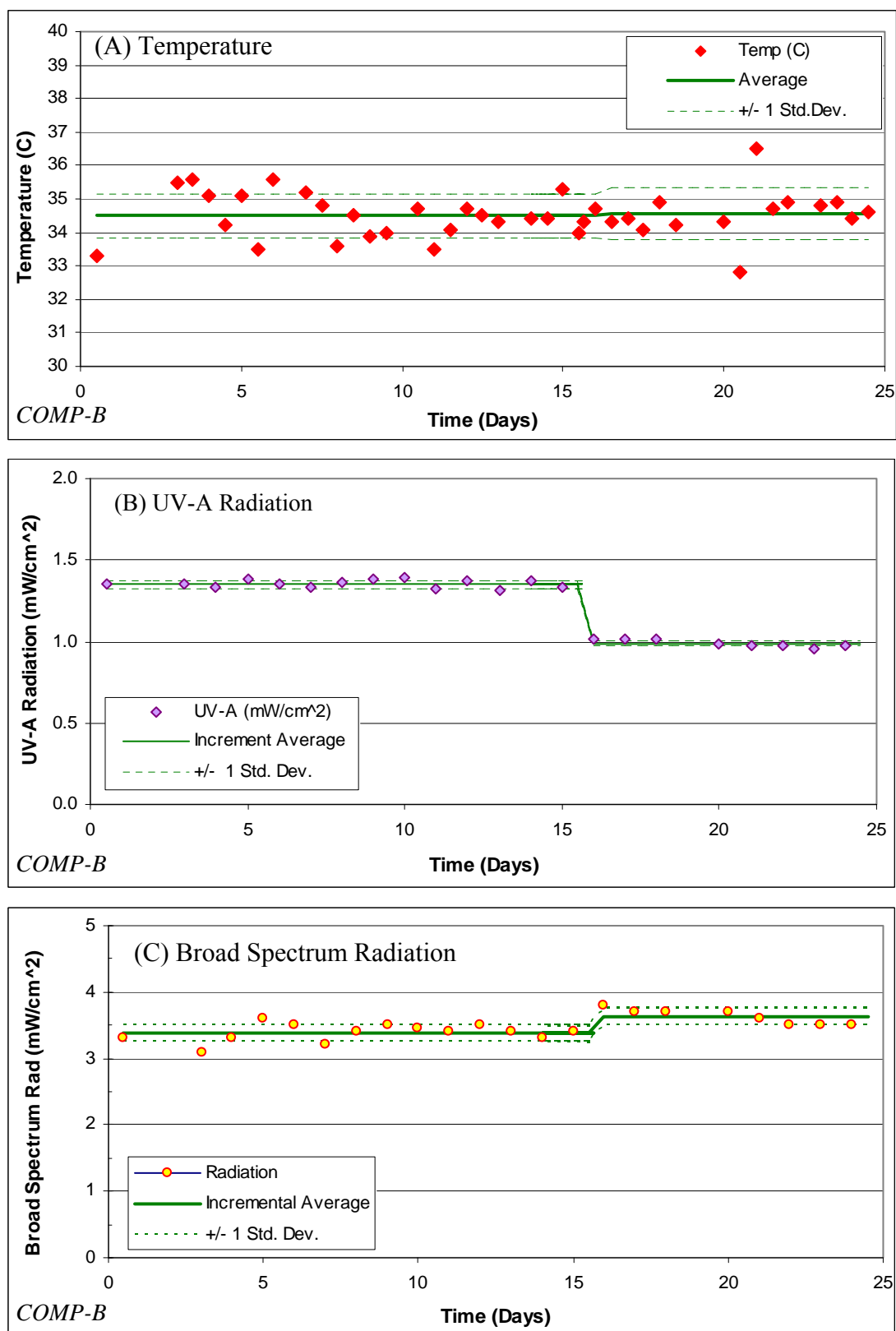


Figure 23. Temporal trends in (A) temperature, (B) UV-A radiation, and (C) Broad spectrum radiation during evaluation of TiO₂-amended Comp-B. Symbols indicate measurements; solid lines indicate period averages; dashed lines delineate ± 1 standard deviation. Small step at day-16 reflects replacement of one UV-A bulb with a UV-B bulb (effect minimal).

Mass Changes in Comp-B TiO₂ Suite. The averaged mass losses from the unamended and amended suites were virtually identical at 0.0045 g (Table 9). TiO₂ is effectively insoluble so the majority of the mass loss is attributed to explosives dissolution.

Column effluent was not analyzed for tungsten, so the degree to which the WO₃ doping agent might have been leached is unknown. But WO₃ could not account for more than approximately 0.0018 g (3% of 0.0608 g amendment), even in the exceedingly unlikely event that all WO₃ were leached from the tablet.

Table 9. Summary of mass changes in Composition B amended with 5 volume-% TiO ₂				
Sample		Initial Mass ¹ (g)	Mass Loss ² (g)	Percent Mass Loss
Unamended	TBA	0.4965	0.0047	0.95%
	TBB	0.4957	0.0045	0.91%
	TBC	0.4968	0.0042	0.85%
		Avg. ± Std. Dev.:	0.0045 ± 0.0003	0.90 ± 0.05%
TiO ₂ -Amended	Ti-A	0.5563	0.0041	0.75%
	Ti-B	0.5557	0.0044	0.79%
	Ti-C	0.5561	0.0051	0.92%
		Avg. ± Std. Dev.:	0.0045 ± 0.0005	0.82 ± 0.09%
¹ Initial tablet mass determined by weight gain to column during construction.				
² Final tablet mass obtained by direct measurement after recovery and drying.				

Supplemental Observations

Two additional observations are worthy of note: (1) the amendment of powdered, unencapsulated, sodium hydroxide aggressively degraded Comp-B, and (2) even small amounts of powdered iron imparts a magnetic property to explosives formulations. These topics were not pursued in detail as they are secondary to the self-remediation questions, and were not part of the original. However, results of some preliminary tests are reported below.

Sodium Hydroxide. Explosives are susceptible to degradation by alkaline hydrolysis (Davis *et al.* 2007). Research to date has centered on application of a basic solutions (*e.g.*, NaOH) or solid compounds (*e.g.*, lime) to explosives-contaminated solutions or soils, never as a self-remediation amendment to explosives.

Composition-B was amended with 5 vol%, powdered, sodium hydroxide (NaOH pellets; 97% from Reagents, Inc., Charlotte NC). However, during the pressing of mixture, the Comp-B tablet was severely altered (Figure 24). NaOH is hygroscopic, so even in a lab with a dehumidifier enough ambient air moisture appears to have been absorbed during preparation to induce the severe degradation. Preparation temperature did not exceed the melting point of NaOH (318 °C). The NaOH-amended tablet was unstable, having oozed a dark brown liquid around the die press plates, precluding further experimentation.

These preliminary results suggest that crystalline NaOH, or another strong base, might be worth pursuing as a self-remediation additive *if the amendment could be safely encapsulated* to prevent immediate absorbance of moisture prior to environmental exposure. As this investigation has demonstrated, addition of a small amount of perishable amendment may not be sufficient to degrade the tremendous excess of explosives present in a munitions round. However, small amounts may be sufficient to either initiate degradation of low-order detonation fragments, or to degrade the charge sufficiently so that detonation characteristics would be severely diminished, reducing the possibility of reusing UXOs in improvised explosive devices (IEDs).



Figure 24. One Comp-B preparation was amended with unencapsulated, powdered NaOH (right disk), but proved too reactive during casting for self-remediation testing.

Magnetic Properties. Iron is a ferromagnetic metal, which means that it may form a permanent magnet and/or be attracted to a permanent magnet. The amendment of powdered carbonyl iron to explosives formulations imparts a potentially useful magnetic characteristic, supporting one of the original hypotheses of this investigation.

The magnetic properties of the Fe-amended explosives were not examined in any quantitative fashion. However, the Comp-B preparation with 5 vol% is readily picked up and held edgewise (Figure 25) with a small neodymium magnet (General Tools, Model 582; 2 lb pickup limit). Likewise, the magnet tool could pick up Fe-amended PBXN-107 samples with as little as 5 wt% (~1 vol%).

It is reasonable to hypothesize that small Fe-bearing fragments resulting from low order detonations would be attracted to a strong magnet, such as those used in common practice to sweep construction sites for extraneous nails and metal fragments. In addition to the amount of Fe⁰ amended, several key variables that may influence magnetic recovery of explosives particles from range soils would include the following: (1) explosives fragment particle size distribution; (2) soil type and condition; (3) persistence of iron amendments before oxidation to non-magnetic oxyhydroxides; and (4) interference from other ferromagnetic soil minerals or allochthonous fragments such as debris from targets or shells. The minimum required amendment for magnetic separation of explosives fragments from soils is unknown. If cleanup of explosives source areas is a priority, magnetic recovery of Fe-bearing explosives fragments could increase the efficacy of any subsequent, in-situ, chemical treatment of the residual soils (e.g. lime application), if necessary.



Figure 25. Comp-B tablet amended with 5 vol% powdered iron is picked up and held with a small magnetic tool (General Tools, Model 582). The PBXN-107 with ~1 vol% (5 wt%) Fe also could be picked up.

[This magnetic tool is TrueValue model 582; <http://www.idealtruevalue.com/servlet/the-136781/Magnetic-Pickup-fdsh-Light/Detail>]

CONCLUSIONS & IMPLICATIONS

The amendments evaluated in PBXN-107 (Fe, FeNi, and TiO₂) and Composition-B (Fe, TiO₂, and dithionite) do not appear to be effective candidates for explosives self-remediation formulations. TNT degradation products attributable to the amendments were detected at low levels while the vast majority of dissolved TNT and RDX remained intact.

All three amendments to PBXN-107 interfered with the curing of the acrylic binder. As a result, all samples were friable to varying degrees, generally in proportion to the amount of amendment. The compromised condition precludes meaningful comparison among replicates and between treatments. However, samples were deemed adequate to test for potential enhanced RDX reactivity with amendments. No RDX reaction products were indicated by standard HPLC analysis methods. Whether and how the acrylic binder in PBXN-107 can be modified to accommodate particulate self-remediation amendments is unknown.

Impact tests reveal a reduction in drop height for amended PBXN-107, suggestive of increased sensitivity. However, no reactions were detected in BAM and ABL friction tests or in the electrostatic tests with PBXN. Composition B samples were not subjected to sensitivity tests.

Uniform masses of Composition B were amended with 5 volume-percent of three separate amendments with no detectable interference with sample cohesion. Chemical reduction of TNT to the 4-amino-DNT intermediate was observed with the dithionite amendment and, to a lesser degree, with the powdered iron amendment. A small increase in TNB (1,3,5-trinitrobenzene), a common photodegradation product, was observed with Comp-B amended with the anatase photocatalyst.

An exploratory test of an unencapsulated, powdered NaOH proved too reactive to evaluate for self-remediation potential. Encapsulated NaOH may have potential as an amendment designed to degrade detonation properties. Powdered Fe amendments to the Comp-B (5 vol%) and PBXN (5 wt% \approx 1 v%) imparts a magnetic property that might be exploitable in range cleanup.

The limited scope of this investigation did not permit exploration as to *why* these particular amendments failed to induce substantial RDX/TNT transformations. Speculations have been offered in the preceding discussions, but the simplest explanation may be that the reactive capacity of the amendments was overwhelmed by the tremendous excess of explosive reactants available in close proximity. It is conceivable that the amendments were occluded by binding agents, polymerizing or surface-binding reaction products, and/or formation of effectively opaque products at the sample surface. Whether the limited degradation observed is sufficient to promote explosives-degrading microbial populations near munitions fragments must be deferred until more effective amendments are developed.

Transition Plan

This pioneering investigation is the first to explore alternative approaches to explosives self-remediation by incorporating reactive amendments. As such, regardless of the disappointing outcome, it will direct future development along more fruitful paths. Lessons learned will guide the selection of alternative amendments, target munitions, experimental procedures, and realistic goals. Self-remediation and munitions deterioration remain valuable goals worth pursuing.

Some of the severe challenges involved are now defined more clearly. The most severe constraint of very small permissible volumes for any non-energetic amendment may prove to be an insurmountable challenge. Although only low levels of degradation were indicated in some

of the experiments, alternative amendments may prove more successful. Many potential reactants, photocatalysts, and perhaps microbes remain to be evaluated as self-remediation amendments.

Elucidation of why any particular self-remediation amendment is effective (or not) should be considered in future experimental designs. A more detailed characterization of the materials at all stages of exposure could provide essential insights. Examination by scanning electron microscopy (SEM), optical petrography, and X-ray diffraction (XRD), among other tools, should provide insights as to the nature of environmental weathering, particularly with respect to the condition and fate of amendments.

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APPENDICIES

A. Supporting Data. All critical supporting data are presented graphically or numerically in the body of the report.

B. List of Scientific/Technical Publications.

McGrath, C.J., and R. Damavarapu (2009). Explosives self-remediation with metal and oxide additives (poster), *SERDP-ESTCP Partners Symposium*, Washington, DC, 1-3 December.

Manuscript on the Comp-B evaluations is in preparation for peer-reviewed journal.